Physics Lib

VOLUME 35 SECOND SERIES NUMBER 5

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

THE AMERICAN PHYSICAL SOCIETY

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PUBLISHED BY THE AMERICAN PHYSICAL SOCIETY

PUBLICATION OFFICE: 450-454 ahnaip street, menasha, wis.

EDITORIAL OFFICE: RIDGE LABORATORY, SCHENECTADY, N. Y.

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THE PHYSICAL REVIEW

Published by the American Physical Society at 450 Ahnaip St., Menasha, Wis. Executive office: University of Minnesota, Minneapolis, Minn. Two volumes annually, twelve issues per volume.

First series. From July 1, 1893, to January 1, 1913, the REVIEW was conducted by Edward L. Nichols, Ernest Merritt and Frederick Bedell, with the financial support of Cornell University. The first four volumes were issued annually; subsequent volumes, semi-annually; thirty-five volumes in all.

Second series. On January 1, 1913, the REVIEW was transferred to the American Physical Society as announced on the first page of the new series which was then begun. Since then it has been conducted by a Board of Editors elected by the Society. Semi-annual volumes begin in January and July. Since July 1, 1929, the REVIEW has been issued twice a month.

Contributors are referred to page 2 of the advertisements for further information.

Annual Subscription, throughout the Postal Union, $10.00 in advance.

Single copies of current volume, $.60.

General index, 1893-1920, $4.00, in advance.

Back Volumes, $6.00 per volume; Back Numbers, $1.00 per copy for issues prior to July 1, 1929 (Vols. 1-33), $.60 per copy for issues subsequent thereto. Postage is free if remittance accompanies order; otherwise postage is extra. No bound volumes can be supplied. The REVIEW offers to purchase a limited number of First Series, Vol. 1, No. 1 (at $2.00 each); Second Series, Vol. 7, No. 1, January 1916; Vol. 7, No. 2, February 1916; Vol. 7, No. 4, April 1916; and Vol. 7, No. 5, May 1916 (at $2.00 each).

Advertisements. Rates will be supplied by the Editor on request. Copy for each number must be received at Minneapolis two weeks prior to the dates of issue; old copy is used until new copy is received. Send electrotypes direct to the printers, George Banta Publishing Co., Menasha, Wis.

Discount of ten percent is allowed subscription agencies and members of the American Physical Society.

Changes of address and Complaints of failure to receive the REVIEW, in the case of members of the Physical Society, should be addressed to the Treasurer; in the case of other subscribers to 450 Ahnaip St., Menasha, Wis.; or to the Editor. New copies can be sent free in response to complaint of non-delivery only if notice of non-delivery is received within three months of date of issue.

Editorial Correspondence should be addressed to the PHYSICAL REVIEW, University of Minnesota, Minneapolis, Minn.

Entered at the postoffice at Menasha, Wis., as second class matter.
Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized September 6, 1926.

Second Series *March 1, 1930* *Vol. 35, No. 5*

THE

PHYSICAL REVIEW

NUCLEAR SPIN AND HYPERFINE STRUCTURE

By H. E. White[1]
Physikalisch-Technische Reichsanstalt, Berlin

(Received January 27, 1930)

Abstract

Assuming that hyperfine structure in spectral lines has its origin in the coupling of a nuclear spin with electron resultant J, a comparison between gross structure and hyperfine structure is made from the following relation, $\Delta\nu_g/\Delta\nu_f = m_k/4im_e$. For those atomic systems for which the electron configurations show LS or jj coupling, the agreement with the above equation is quite as good as would be expected. For electronic configurations which do not show LS or jj coupling it is doubtful whether such a comparison of gross structure with hyperfine structure can be suitably made. From the meagre data as yet available, one is led to suspect that nuclear spin is due to the last electrons, protons, or both (most probably electrons) added to the nucleus in atomic construction. These electrons should, in accordance with the principles of the wave-mechanics, have a *probability density* spherically symmetrical about the nucleus. The difference between the electrons associated with the nucleus and the outer electrons is that the nuclear electrons carry with them in space quantization the total mass of the atom.

THE splitting up of ordinary energy levels into a number of hyperfine structure components is quite generally attributed to a nuclear angular momentum. Observations indicate that this nuclear spin, whether due to electrons, protons, or to both electrons and protons, carries with it in space quantization the total mass of the nucleus. Assuming the nuclear spin to be a rotation of the nucleus as a whole, Jackson[2] has derived the following equation for the approximate shift in energy of ordinary energy levels due to nuclear spin.

$$\Delta\nu_g/\Delta\nu_f = m_k/2m_e. \tag{1}$$

Here $\Delta\nu_g$ is a gross or multiplet structure separation, $\Delta\nu_f$ the corresponding hyperfine structure separation, m_e the mass of an electron and m_k the mass of the nucleus. Since this formula was derived for a nuclear spin of $i=\frac{1}{2}$ a quantum of energy, it may be made general for all values of i by replacing the constant 2 in the above equation with $4i$. This gives

[1] National Research Fellow.
[2] Jackson, Proc. Roy. Soc. **A121**, 432 (1928).

$$\Delta\nu_g/\Delta\nu_f = m_k/4im_e \tag{2}$$

which for $i=\frac{1}{2}$ reduces to equation (1).

Jackson has shown[2] that in the simple case of a so called *one electron system*, like caesium, an electron spin doublet separation ($\Delta\nu_g$), for example $^2P_{1/2}-{}^2P_{3/2}(6p)$, is to be compared with the hyperfine separation ($\Delta\nu_f$) of one of the terms, ^2P. The ratio $\Delta\nu_g/\Delta\nu_f$, as compared with computed values from Eqs. (1) and (2), is in reality in quite good agreement (Table I).

From a discussion with Dr. Schüler[3] it appears that the hyperfine structure of λ5486, $^3S_1-{}^3P_{0,1,2}$, in singly ionized lithium may be accounted for by assigning an angular momentum, $i=\frac{1}{2}$, to the nucleus of Li.[7] From the observed hyperfine structure, the $^3S_1(1s2s)$ term and the $^3P_2(1s2p)$ term have normal doublet separations of about 0.60 cm^{-1} and 0.45 cm^{-1} respectively (error ± 0.10 cm^{-1}). The splitting up of these terms is shown in Fig. 1. In

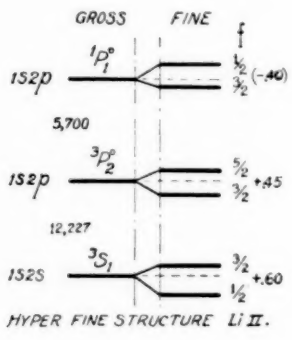

Fig. 1.

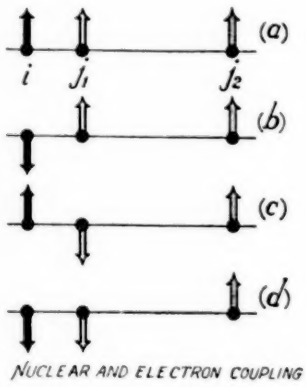

Fig. 2.

this case of a nucleus and two electrons, it may be shown by the use of Fig. 2 which gross structure and which hyperfine structure separations are to be compared with each other. The left hand vector i, in Fig. 2, may be taken to represent the nucleur angular momentum, $\frac{1}{2}$, of Li,[7] and j_1 and j_2 may be taken to represent $1s$ and $2p$ electrons respectively. In the space quantization of these three vectors the coupling between j_1 and j_2 produces the gross-structure energy levels, whereas the coupling between j_1 and i and between j_2 and i produces the hyperfine energy levels. For the term $_{5/2}{}^3P^0{}_2$ of Fig. 1, all three vectors i, j_1 and j_2, Fig. 2(a), are parallel as shown.[4] When i is now inverted, to position Fig. 2(b), the shift in energy to the term $_{3/2}{}^3P^0{}_2$ is observed to be about 0.45 cm^{-1}. Owing to the relative nearness of the $1s$ electron

[3] Schüler, Zeits. f. Physik.

[4] With the apparent need of the new quantum number f to represent an energy level, it is suggested that this quantum number preceed the ordinary term designation as a subscript for example, $_{3/2}{}^3D^0{}_2$. If the electron configuration is given, it is desirable to include the nuclear spin, for example, $i_{5/2}4s3d$. A radiated hyperfine structure line would be designated, $_{3/2}{}^3S_1-{}_{5/2}{}^3P^0{}_2$.

to the nucleus, this shift in energy is almost entirely due to the coupling between j_1 and i. When from ${}_{5/2}{}^3P^\circ{}_2$, Fig. 2(a), the vector j_1 is inverted to position Fig. 2(c), the shift in energy to ${}_{3/2}{}^1P_1$ is observed to be about -7000 cm^{-1}. The inversion now of i to position ${}_{1/2}{}^1P_1$, Fig. 2(d), should produce, although not yet observed, a shift of about -0.4 cm^{-1}. The inverted hyperfine structure in this ${}^1P_1$ term follows from the hypothesis that, while the separation arises from the coupling between j_1 and i, space quantization must take place between nuclear spin, i, and electron resultant, J.[5] The ratio $\Delta\nu_g/\Delta\nu_f$ is given in Table I along with the values obtained for other elements.

Making quite the same arguments given above for lithium, a correlation between gross structure and hyperfine structure may be made for an atomic system having a number of valence electrons, for example, manganese, Mn I. Using again Fig. 2, vector i is taken to represent the nuclear angular momentum $i=5/2$ of manganese, vector j_1 to represent a $4s$ electron and, vector j_2 to represent the resultant angular momentum of all of the rest of the electrons outside of the nucleus, for example $3d^6$, ${}^5D_4$, of Mn II. With all three vectors parallel as in Fig. 2(a) the atom is in state ${}_7{}^6D_{9/2}(i_{5/2}3d^64s)$. The inversion of vector i to position (b), ${}_2{}^6D_{9/2}(i_{5/2}3d^64s)$, produces a shift in energy of about 0.50 cm^{-1}. An inversion, however of vector j_1 from position (a) to position (c), ${}_6{}^4D_{7/2}(i_{5/2}3d^64s)$, produces a shift in energy of $-6{,}244$ cm^{-1}. The ratio $\Delta\nu_g/\Delta\nu_f=12{,}488$ is in quite good agreement with the calculated value 10,100.

In order to account for the observed hyperfine structure of the principal doublet of caesium, Jackson[2] assigned an angular momentum of $i=\frac{1}{2}$ to the nucleus of caesium. It is interesting to note that the observations are equally well explained by assuming greater values of i. From values of nuclear spin found in other elements 1/2, 5/2 and 9/2, and the last two columns of Table I, excluding Tl and Cd, the value $i=5/2$ seems to be, although the evidence is not strong, the more probable for caesium.

TABLE I.
A comparison of gross structure with hyperfine structure.

Element	i	Electron Config.	Terms	$\Delta\nu_g$	$\Delta\nu_f$	$\Delta\nu_g/\Delta\nu_f$	$m_k/4im_e$
Li^7 II	$\frac{1}{2}$	$1s2p$	${}^3P_2^\circ-{}^1P_1^\circ$	7,000	0.45	15,555	6,440
Mn I	$2\frac{1}{2}$	$3d^64s$	${}^6D_{4\frac{1}{2}}-{}^4D_{3\frac{1}{2}}$	6,244	.50	12,488	10,100
Mn I	$2\frac{1}{2}$	$3d^54p4s$	${}^8S_{3\frac{1}{2}}^\circ-{}^6S_{2\frac{1}{2}}^\circ$	9,984	.60	16,640	10,100
Cs I	$\frac{1}{2}$?	$6p$	${}^2P_{\frac{1}{2}}^\circ-{}^2P_{1\frac{1}{2}}^\circ$	554	.01	55,400	122,000
Cs I	$2\frac{1}{2}$?	$6p$	${}^2P_{\frac{1}{2}}^\circ-{}^2P_{1\frac{1}{2}}^\circ$	554	.01	55,400	24,500
Cs I	$4\frac{1}{2}$?	$6p$	${}^2P_{\frac{1}{2}}^\circ-{}^2P_{1\frac{1}{2}}^\circ$	554	.01	55,400	13,600
Tl I	$\frac{1}{2}$	$6p$	${}^2P_{\frac{1}{2}}^\circ-{}^2P_{1\frac{1}{2}}^\circ$	7,793	.40	19,480	187,600
Tl II	$\frac{1}{2}$	$6s6p$	${}^3P_2^\circ-{}^1P_1^\circ$	13,935	3.5	3,980	187,600
Cd I	$\frac{1}{2}$	$5s5p$	${}^3P_2^\circ-{}^1P_1^\circ$	11,864	.25	47,460	103,000

The ratios $\Delta\nu_g/\Delta\nu_f$, given in Table I for Tl I and Tl II, are decidedly not in agreement with the calculated value 187,600. From Zeeman effect data on λ3776 of Tl I[6] the nuclear spin is quite certainly 1/2. The enormous hyperfine

[5] H. E. White, Phys. Rev. **34**, 1404 (1929).
[6] Schüller and Brück, Zeits. f. Physik **56**, 291 (1929).

structure separations in Tl II as compared with the small separations found in Tl I are undoubtedly due to the strong coupling between i and the deep penetrating $6s$ electron for Tl II, in contrast with the coupling and penetration of a $6p$ electron in Tl I. In Tl II, it would appear that the difficulty arises in the uncertainty of the coupling between the two valence electrons. Since the terms do not indicate either LS or jj coupling, it is doubtful whether such a comparison of gross structure with hyperfine structure can be suitably made for such cases. It has been interesting to note, however, for all observed hyperfine structure, that the space quantization between electron resultant J and the nuclear spin i always follows the interval rule, i.e., a Ji coupling where the intervals are proportional to cos Ji. The exact form of the constant multiplier of i in equation (2) depends largely upon the distribution of charge causing the nuclear spin. Even with the meagre data as yet available, one is led to suspect that the nuclear spin is due to the last added electrons, protons, or both electrons and protons. From observations electrons alone seem to be the most probable.[5] These electrons should, in accordance with the principles of the wave mechanics, have a probability density spherically symmetrical about the nucleus and might be thought of as a charged shell over the surface of the nucleus. The difference between the electrons associated with the nucleus and the outer electrons is that the nuclear electrons carry with them in space quantization the total mass of the atom.

The author wishes to take this opportunity to thank Dr. Paschen for his interest in and criticism of this paper.

THE SECOND SPARK SPECTRUM OF ANTIMONY AND A NOTE ON THE FIRST SPARK SPECTRUM OF TIN

By R. J. Lang
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(Received January 30, 1930)

Abstract

Some sixty lines of the vacuum spark spectrum of antimony have been classified as transitions between the following terms of Sb III: $(s^2 5p)^2P$, $(s^2 6p)^2P$, $(s^2 6s)^2S$, $(s^2 7s)^2S$, $(s^2 8s)^2S$, $(s^2 5d)^2D$, $(s^2 6d)^2D$, $(s^2 4f)^2F$, $(s^2 5f)^2F$, $(s^2 5g)^2G$, $(s^2 6g)^2G$, $(s5p^2)^4P$, ^2D, ^2S, ^2P and $(5p^3)^4S$. Corresponding to the deepest term value an ionization potential of approximately 24.7 volts is calculated. A note on SN II gives the terms ^4P and ^2S from the $(s5p^2)$ configuration and new value for the terms: $(s^2 7s)^2S$, $(s^2 8s)^2S$, $(s^2 7d)^2D$ and $(s^2 6f)^2F$.

THE vacuum spark spectrum of antimony has been measured over the range 6600 to 600A and also the Paschen hollow-cathode spectrum from 5200 to 1950A. By means of these two measurements it has been possible to separate the first and second spark spectra rather definitely from one another and thus to arrive at a classification for the latter. Work on the first spark spectrum is now in progress and will be reported on later. The measurements of the vacuum spark spectrum below 2500A were made on a two-meter grating mounted in a vacuum spectrograph giving a dispersion of 4.5A per mm. Above 2000A several instruments were used. The vacuum spark and hollow cathode spectra were measured in Edmonton on a two-meter Rowland grating kindly loaned to the author by Professor Smith. The vacuum spark spectrum was also measured in Michigan by the author using a Hilger E_2 quartz spectrograph made available through the courtesy of the Department of Physics. The author is also indebted to Professor R. A. Sawyer of Michigan for a plate of the vacuum spark in the region from 5300 to 6600A made on a large Hilger glass spectrograph. A few wave-lengths are taken also from Schippers measures given by Kayser.

In a previous report[1] the author gave three multiplets for Sb III all of which turn out to be real but the first one given was improperly classified as $(s^2 6s)^2S-(s^2 6p)^2P$. It should have been $(s5p^2)^2S-(s^2 6p)^2P$. It thus corresponds very satisfactorily to the doublet in As III at 4200A. A paper on As III and Sb III appeared later in the Indian Journal of Physics.[2]

Some important electron configurations and resultant terms expected in the spectrum of Sb III are as follows:

[1] Lang, Phys. Rev. **32**, 737 (1928).
[2] Pattabhiramiah and Rao, Indian Journ. Phys. **3**, 437, 1929

Configuration	Terms	Configuration	Terms
$(s^2 5p)$	^2P	$(s5p^2)$	$^4P, {}^2PDS$
$(s^2 6s)$	^2S	$(s5p5d)$	$^4PDF, {}^2PDF$
$(s^2 5d)$	^2D	$(s5p6s)$	$^4P {}^2P$
$(s^2 4f)$	^2F	$(5p^3)$	$^4S, {}^2PD$
$(s^2 5g)$	^2G	$(s5p6p)$	$^4PSD, {}^2SPD$

TABLE I. *Empirical term values in Sb III.*

Odd Terms			Even Terms		
$(s^2 5p)^2P_{\frac{1}{2}}$	200272	6576	$(s5p^2)^2D_{1\frac{1}{2}}$	123744	1270
$(s^2 5p)^2P_{1\frac{1}{2}}$	193696		$(s5p^2)^2D_{2\frac{1}{2}}$	122474	
$(s^2 4f)^2F_{2\frac{1}{2}}$	118940	373	$(s^2 6s)^2S_{\frac{1}{2}}$	107321	
$(s^2 4f)^2F_{3\frac{1}{2}}$	118567		$(s5p^2)^2S_{\frac{1}{2}}$	106852	
$(s^2 6p)^2P_{\frac{1}{2}}$	85550	1668	$(s5p^2)^2P_{\frac{1}{2}}$	105624	5392
$(s^2 6p)^2P_{1\frac{1}{2}}$	83882		$(s5p^2)^2P_{1\frac{1}{2}}$	100232	
$(s^2 5f)^2F_{3\frac{1}{2}}$	64055	−55	$(s^2 5d)^2D_{1\frac{1}{2}}$	101450	1567
$(s^2 5f)^2F_{2\frac{1}{2}}$	64000		$(s^2 5d)^2D_{2\frac{1}{2}}$	99883	
$(5p^3)^4S_{1\frac{1}{2}}$	51259		$(s^2 7s)^2S_{\frac{1}{2}}$	57143	
Even Terms			$(s^2 6d)^2D_{1\frac{1}{2}}$	55589	237
			$(s^2 6d)^2D_{2\frac{1}{2}}$	55352	
$(s5p^2)^4P_{\frac{1}{2}}$	145906	3596	$(s^2 8s)^2S_{\frac{1}{2}}$	36882	
$(s5p^2)^4P_{1\frac{1}{2}}$	142310	5358	$(s^2 5g)^2G$	35966	
$(s5p^2)^4P_{2\frac{1}{2}}$	136952		$(s^2 6g)^2G$	25812	

TABLE II. *Comparison of term values.*

Term	Element	4	5	6	7	8
	In I			22295	10366	6031
^2S	Sn II			15205	7841	5194
	Sb III			11924	6349	4098
	In I		46668	14811	7808	
$^2P_{\frac{1}{2}}$	Sn II		29426	11553		
	Sb III		22252	9506		
	In I		13775	7620	4832	
$^2D_{1\frac{1}{2}}$	Sn II		11575	6867	4342	
	Sb III		11272	6176		
	In I		6960			
$^2F_{2\frac{1}{2}}$	Sn II		7104	4511		
	Sb III	13215	7111			
	In I					
^2G	Sn II					
	Sb III		3996	2868		

TABLE III. *Combinations, intensities and discrepancies in the spectrum of Sb III.*

Odd Terms / Even Terms	$(s^2 5p)^2P_{\frac{1}{2}}$	$(s^2 5p)^2P_{1\frac{1}{2}}$	$(s^2 4f)^2F_{2\frac{1}{2}}$	$(s^2 4f)^2F_{3\frac{1}{2}}$	$(s^2 6p)^2P_{\frac{1}{2}}$	$(s^2 6p)^2P_{1\frac{1}{2}}$	$(s^2 5f)^2F_{3\frac{1}{2}}$	$(s^2 5f)^2F_{2\frac{1}{2}}$	$(5p^3)^4S_{1\frac{1}{2}}$
	200272	193696	118940	118567	85550	83882	64055	64000	51259
$(s5p^2)^4P_{\frac{1}{2}}$ 145906	12 2	2 1							10 −2
$(s5p^2)^4P_{1\frac{1}{2}}$ 142310	15 −2	10 −2							10 −4
$(s5p^2)^4P_{2\frac{1}{2}}$ 136952		12 0							12 0
$(s5p^2)^2D_{1\frac{1}{2}}$ 123744	20 1	10 −1			12 5	5 3		15 −3	8 1
$(s5p^2)^2D_{2\frac{1}{2}}$ 122474		20* −6				15 5	15 −2 *	3 −3	20* 1
$(s^2 6s)^2S_{\frac{1}{2}}$ 107321	30 1	40 0			30 0	40 0			
$(s5p^2)^2S_{\frac{1}{2}}$ 106852	20 0	30 0			30 0	50 0			
$(s5p^2)^2P_{\frac{1}{2}}$ 105624	10 −3	10 0							
$(s^2 5d)^2D_{1\frac{1}{2}}$ 101450	40 −2	20 0	1 −4	3 −15?	3 0	1 −1		20 0	
$(s5p^2)^2P_{1\frac{1}{2}}$ 100232	15 −2	20 0							
$(s^2 5d)^2D_{2\frac{1}{2}}$ 99883		40 4	1 −6			5 3	20 0	5 1	
$(s^2 7s)^2S_{\frac{1}{2}}$ 57143	10 −3	15 −3			15 1	30 −1			
$(s^2 6d)^2D_{1\frac{1}{2}}$ 55589	10 −3	8 −2			20 1	15 0			
$(s^2 6d)^2D_{2\frac{1}{2}}$ 55352		15 −4				50 0			
$(s^2 8s)^2S_{\frac{1}{2}}$ 36882					3 0	5 0			
$(s^2 5g)^2G$ 35966			50 0	50 0			40 −1	40 −1	
$(s^2 6g)^2G$ 25812			5 3	5 0			1 −2	1 3	

* Classified twice.

TABLE IV. *Classified lines of Sb III.*

Classification	λ(I.A.)	I	ν
$(s^25p)^2P_{\frac{1}{2}} - (s^26d)^2D_{1\frac{1}{2}}$	691.18	10	144680
$^2P_{1\frac{1}{2}} - \quad ^2D_{2\frac{1}{2}}$	722.86	15	138340
$^2P_{1\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	724.81	8	138105
$(s^25p)^2P_{\frac{1}{2}} - (s^27s)^2S_{\frac{1}{2}}$	698.69	10	143126
$^2P_{1\frac{1}{2}} - \quad ^2S_{\frac{1}{2}}$	732.33	15	136550
$(s^25p)^2P_{\frac{1}{2}} - (s5p^2)^2P_{1\frac{1}{2}}$	999.62	15	100038
$^2P_{\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	1056.58	10	94645
$^2P_{1\frac{1}{2}} - \quad ^2P_{1\frac{1}{2}}$	1069.93	20	93464
$^2P_{1\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	1135.43	10	88072
$(s^25p)^2P_{\frac{1}{2}} - (s^25d)^2D_{1\frac{1}{2}}$	1011.94	40	98820
$^2P_{1\frac{1}{2}} - \quad ^2D_{2\frac{1}{2}}$	1065.90	40	93817
$^2P_{1\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	1084.06	20	92246
$(s^25p)^2P_{\frac{1}{2}} - (s5p^2)^2S_{\frac{1}{2}}$	1070.43	20	93420
$^2P_{1\frac{1}{2}} - \quad ^2S_{\frac{1}{2}}$	1151.49	30	86844
$(s5p^2)^4P_{2\frac{1}{2}} - (5p^3)^4S_{1\frac{1}{2}}$	1056.58	10	94645
$^4P_{1\frac{1}{2}} - \quad ^4S_{1\frac{1}{2}}$	1098.34	10	91047
$^4P_{\frac{1}{2}} - \quad ^4S_{1\frac{1}{2}}$	1166.96	12	85693
$(s^24f)^2F_{2\frac{1}{2}} - (s^26g)^2G$	1073.76	5	93131
$^2F_{3\frac{1}{2}} - \quad ^2G$	1078.10	5	92755
$(s^25p)^2P_{\frac{1}{2}} - (s^26s)^2S_{\frac{1}{2}}$	1075.82	30	92952
$^2P_{1\frac{1}{2}} - \quad ^2S_{\frac{1}{2}}$	1157.74	40	86375
$(s^24f)^2F_{2\frac{1}{2}} - (s^25g)^2G$	1205.20	50	82974
$^2F_{3\frac{1}{2}} - \quad ^2G$	1210.64	50	82601
$(s^25p)^2P_{\frac{1}{2}} - (s5p^2)^2D_{1\frac{1}{2}}$	1306.69	20	76529
$^2P_{1\frac{1}{2}} - \quad ^2D_{2\frac{1}{2}}$	1404.18	20	71216
$^2P_{1\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	1429.57	10	69951
$(s5p^2)^2D_{1\frac{1}{2}} - (5p^3)^4S_{1\frac{1}{2}}$	1379.58	8	72486
$^2D_{2\frac{1}{2}} - \quad ^4S_{1\frac{1}{2}}$	1404.18	20	71216
$(s5p^2)^2D_{1\frac{1}{2}} - (s^25f)^2F_{2\frac{1}{2}}$	1673.89	15	59741
$^2D_{2\frac{1}{2}} - \quad ^2F_{2\frac{1}{2}}$	1710.23	3	58472
$^2D_{2\frac{1}{2}} - \quad ^2F_{3\frac{1}{2}}$	1711.84	15	58417
$(s^25p)^2P_{\frac{1}{2}} - (s5p^2)^4P_{1\frac{1}{2}}$	1725.33	15	57960
$^2P_{1\frac{1}{2}} - \quad ^4P_{2\frac{1}{2}}$	1762.30	12	56744
$^2P_{\frac{1}{2}} - \quad ^4P_{\frac{1}{2}}$	1839.32	12	54368
$^2P_{1\frac{1}{2}} - \quad ^4P_{1\frac{1}{2}}$	1946.13	10	51384
$^2P_{1\frac{1}{2}} - \quad ^4P_{\frac{1}{2}}$	2091.85	2	47791
$(s^26p)^2P_{\frac{1}{2}} - (s^28s)^2S_{\frac{1}{2}}$	2054.10	3	48668
$^2P_{1\frac{1}{2}} - \quad ^2S_{\frac{1}{2}}$	2127.00	5	47000
$(s5p^2)^2D_{1\frac{1}{2}} - (s^26p)^2P_{1\frac{1}{2}}$	2507.71	5	39865
$^2D_{2\frac{1}{2}} - \quad ^2P_{1\frac{1}{2}}$	2590.13	15	38597
$^2D_{1\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	2617.17	12	38199
$(s^25f)^2F_{3\frac{1}{2}} - (s^26g)^2G$	2614.20	1	38241
$^2F_{2\frac{1}{2}} - \quad ^2G$	2617.63	1	38191
$(s^25d)^2D_{1\frac{1}{2}} - (s^25f)^2F_{2\frac{1}{2}}$	2669.39	20	37450
$^2D_{2\frac{1}{2}} - \quad ^2F_{2\frac{1}{2}}$	2785.87	5	35884
$^2D_{2\frac{1}{2}} - \quad ^2F_{3\frac{1}{2}}$	2790.27	20	35828

TABLE IV (*Continued*)

Classification	λ(I.A.)	I	ν
$(s^2 6p)^2P_{\frac{1}{2}} - (s^2 6d)^2D_{1\frac{1}{2}}$	3336.61	20	29962
$^2P_{1\frac{1}{2}} - \quad ^2D_{2\frac{1}{2}}$	3504.07	50	28530
$^2P_{1\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	3533.45	15	28293
$(s^2 6p)^2P_{\frac{1}{2}} - (s^2 7s)^2S_{\frac{1}{2}}$	3519.06	15	28408
$^2P_{1\frac{1}{2}} - \quad ^2S_{\frac{1}{2}}$	3738.90	30	26738
$(s^2 5f)^2F_{3\frac{1}{2}} - (s^2 5g)^2G$	3559.18	40	28088
$^2F_{2\frac{1}{2}} - \quad ^2G$	3566.25	40	28033
$(s^2 6s)^2S_{\frac{1}{2}} - (s^2 6p)^2P_{1\frac{1}{2}}$	4265.09	40	23439
$^2S_{\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	4591.89	30	21771
$(s5p^2)^2S_{\frac{1}{2}} - (s^2 6p)^2P_{1\frac{1}{2}}$	4352.16	50	22970
$^2S_{\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	4692.91	30	21302
$(s^2 4f)^2F_{2\frac{1}{2}} - (s^2 5d)^2D_{2\frac{1}{2}}$	5247.71	1	19051
$^2F_{2\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	5717.3	1	17486
$^2F_{3\frac{1}{2}} - \quad ^2D_{1\frac{1}{2}}$	5845.5	3	17102
$(s^2 5d)^2D_{1\frac{1}{2}} - (s^2 6p)^2P_{1\frac{1}{2}}$	5690.8	1	17567
$^2D_{2\frac{1}{2}} - \quad ^2P_{1\frac{1}{2}}$	6246.7	5	16004
$^2D_{1\frac{1}{2}} - \quad ^2P_{\frac{1}{2}}$	6287.6	3	15900

In Table I the terms which have been located together with the empirical term values and separations are given. All of the term values rest upon an arbitrary choice of 64000 cm^{-1} for the value of $(s^2 5f_{\prime})^2F_{2\frac{1}{2}}$. Experience has shown that one can probably arrive at as good or even better values for the terms by a comparison such as is given in Table II than by the use of a Rydberg formula applied to two P or two S terms such as are available in this instance. The deepest F terms are not absolutely certain since the combination with the deepest normal D terms is not very satisfactory. The same may also be true of the second G terms and the third S terms, the last depending upon one combination only since no others fall within the range of measurements. Hence until some of these terms can be established more certainly it seemed as well to estimate the value of the basic term.

In Table III the intensities of observed combinations are shown and under each intensity the discrepancy between the observed wave-number and the wave-number calculated from the values assigned to the energy levels is given. In Table IV a list of all the lines which have been classified in the spectrum of Sb III is given. Throughout this report all wave-lengths above 2000A are given in I.A. (air) below this value in I.A. (vacuum) while all wave-numbers are reduced to vacuum values. Corresponding to the deepest term of this spectrum an ionization potential of 24.7 volts is found.

A NOTE ON SN II

The hollow cathode spectrum of tin was also photographed between 6000A and 2000A in an endeavor to find more terms from the $(s5p^2)$ con-

figuration. Out of the total of nine terms (^4P, ^2D, ^2S, ^2P) arising from this configuration none but ^2D had been located.[3]

The $(s^25p)^2P-(s5p^2)^4P$ multiplet in In I had already been found[4] and those for Sn II and Sb III were located by the use of the doublet laws. The multiplet in Sn II is taken from the spectrum of the hollow cathode. It occurs but very weakly in the vacuum spark spectrum. That for Sb III is taken from the vacuum spark spectrum and the only abnormality is the weak intensity of one of the lines in this multiplet.

TABLE V. *Multiplets and terms in the spectrum of Sn II.*

Configuration	λ(I.A.)	I	ν	Δν	Term values	
$(s^25p)^2P\ ^1_2-(s^27s)^2S_{\frac12}$	1158.21	2	86340		$(s^25p)^2P\ ^1_2$	117704
$^2P_{1\frac12}-\ \ ^2S_{\frac12}$	1218.19	4	82089	4251	$^2P_{1\frac12}$	113451*
$(s^26p)^2P_{\frac12}-(s^28s)^2S_{\frac12}$	3930.37	2	25435		$(s^27s)^2S\ _{\frac12}$	31363
$^2P_{1\frac12}-\ \ ^2S_{\frac12}$	4071.79	2	24552	883		
$(s^25d)^2D_{1\frac12}-(s^26f)^2F$	3537.56	1	28260			
$^2D_{2\frac12}-\ \ ^2F$	3620.54	1	27613	647	$(s^28s)^2S\ _{\frac12}$	20778
$(s^25p)^2P_{1\frac12}-(s5p^2)^2D_{1\frac12}$	1699.50	12	58841	4252	$(s^27d)^2D_{1\frac12}$	17367
$^2P_{1\frac12}-\ \ ^2D_{2\frac12}$	1811.23	15	55211	622*	$^2D_{2\frac12}$	17327
$^2P_{\frac12}-\ \ ^2D_{1\frac12}$	1831.85	12	54589			
$(s5p^2)^2D_{1\frac12}-(s^26f)^2F$	2448.93	1	40821		$(s^26f)^2F$	18043
$^2D_{2\frac12}-\ \ ^2F$	2486.95	2	40197	624		
					$(s5p^2)^4P\ _{\frac12}$	73196
$(s^25p)^2P\ _{\frac12}-(s5p^2)^4P_{1\frac12}$	2151.57	12	46462		$^4P_{1\frac12}$	71242
$^2P_{1\frac12}-\ \ ^4P_{2\frac12}$	2209.70	10	45241	1954	$^4P_{2\frac12}$	68210
$^2P\ _{\frac12}-\ \ ^4P\ _{\frac12}$	2246.11	10	44508			
$^2P_{1\frac12}-\ \ ^4P_{1\frac12}$	2368.26	15	42211	1957	$(s5p^2)^2D_{1\frac12}$	58863
$^2P_{1\frac12}-\ \ ^4P\ _{\frac12}$	2483.48	12	40254		$^2D_{2\frac12}$	58240*
$(s^25p)^2P\ _{\frac12}-(s5p^2)^2S\ _{\frac12}$	1223.73	10	81717			
$^2P_{1\frac12}-\ \ ^2S\ _{\frac12}$	1290.89	20	77465	4252	$(s5p^2)^2S\ _{\frac12}$	35986
$(s^26p)^2P\ _{\frac12}-(s^27d)^2D_{1\frac12}$	3465.73	3	28846	884		
$^2P_{1\frac12}-\ \ ^2D_{2\frac12}$	3570.09	8	28002			
$^2P_{1\frac12}-\ \ ^2D_{1\frac12}$	3575.31	4	27962	40		

* Green and Loring.

The $(s^25p)^2P-(s5p^2)^2D$ multiplet seems well established in Sn II and Sb III. One peculiarity worth mentioning is that the position of this multiplet in the spectrum of Sn II is almost exactly the same as in Si II[5]. However, there seems little doubt that in Sn II this group has been correctly classified[3] for when a tin spark in nitrogen, excited by a 2200 volt transformer joined to the 110 volt A.C. mains, was photographed between 2000A and 1250A but nine tin lines were found including the three lines of this multiplet, and every one of these lines except one (1290.90A) had been classified as arising from transitions involving the deepest ^2P levels of the atom of Sn II.

[3] Green and Loring, Phys. Rev. **30**, 574 (1927).
[4] Lansing, Phys. Rev. **34**, 597 (1929); Sawyer and Lang, Phys. Rev. **34**, 712 (1929).
[5] Fowler, Trans. Roy. Soc. **A225**, 26 (1925).

In regard to the $(s^25p)^2P-(s5p^2)^2S$ doublet it may be stated that the line (1290.90A) together with another line at 1223.79A which occurs in the vacuum spark, but unable here to pass the fluorite window, have the separation of the deepest ^2P terms. There seems little doubt that these two lines represent this doublet as has been suggested.[3]

The remaining $(s^25p)^2P-(s5p^2)^2P$ multiplet in Sn II has not been located with any certainty. There is one possibility worth mentioning, however. The $(s^25p)^2P-(s^27s)^2S$ doublet[3] occurs with too great intensity in the vacuum spark and the ^2S term is greater than one would expect. Another pair of weaker lines, one of which had not been resolved from a stronger tin line, probably represent this doublet and the stronger pair represents one-half of the missing multiplet. However, it must be said that there is not complete agreement yet between Sn II and Sb III in regard to these terms of the $(s5p^2)$ configuration and it does not seem possible to obtain this at the present time. When the arc spectrum of indium has been studied below 2000A it should be possible to obtain this agreement. An attempt to do this is now in progress. One or two other minor alterations have been made in the spectrum of Sn II all of which are shown in Table V.

The author takes this opportunity of thanking the Research Council of Canada for a grant to carry on this research.

THE EMISSION SPECTRUM OF BENZENE IN THE REGION 2500–3000A

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(Received January 25, 1930)

Abstract

The ultra-violet emission band spectrum of benzene vapor has been observed with a Tesla discharge as a means of excitation. The wave-lengths of over 100 bands lying between 2400 and 3000A have been measured with an accuracy of ±0.5A. It is found that the measurements are in general in agreement with those of McVicker, Marsh and Stewart. All the bands except the fainest and most diffuse ones may be represented by the following equations:

$1/\lambda = 37485 + 924m - 161n$ $\quad 1/\lambda = 37425 - 986m - 162n$
$1/\lambda = 37398 + 924m - 162n$ $\quad 1/\lambda = 36479 - 991m - 162n$
$1/\lambda = 37485 - 986m - 162n$ $\quad 1/\lambda = 36412 - 991m - 162n$

where m and n are integers.

The evidence supporting the conclusion that the bands are due to benzene and not to some decomposition product is summarized. The applicability of the data to spectroscopic analysis is also discussed.

Introduction

THE general features of the spectra obtained from the vapor of benzene and its simple derivatives under the excitation of the Tesla discharge have been described by McVicker, Marsh and Stewart,[1] who have designated them as Tesla luminescence spectra to distinguish them from the absorption and fluorescence spectra. The present research was undertaken as an extension of their work; it was hoped, on the purely chemical side, to develop the suggestion made by them that a means of ascertaining the identity and quantity of any impurity present could be elaborated. In this regard it has been shown that such a method would be unwieldy in practice, except perhaps for routine work on a large number of samples; moreover, the number of likely impurities which yield satisfactory spectra under these conditions is rather small. On the other hand, it was felt that more comprehensive data on the Tesla luminescence spectra, particularly on the spectrum of benzene which is noteworthy for the sharpness of its bands and the absence of any continuous background, might be obtained, which with the increased accuracy would lead to some theoretical interpretation of the observed regularities. In this object some success has been achieved and the present work describes the results for benzene; the results for the simple derivatives will be published in the near future.

* From a dissertation presented by J. B. Austin to the Graduate School of Yale University, June 1928, in candidacy for the degree of Doctor of Philosophy.

† Commonwealth Fellow 1926–1928.

[1] McVicker, Marsh and Stewart, J. Chem. Soc. **123,** 642 (1923).

Experimental Method

The methods employed differed from those of McVicker, Marsh, and Stewart in many ways, the most significant difference being the use of much lower pressures of the vapor. They used benzene vapor at pressures as high as 65 mm of Hg and were forced to use a steam jacket to prevent condensation; in the present work the pressures ranged from 0.01 to 0.10 mm which yielded satisfactory results at room temperature. In its final form our apparatus was fitted with internal electrodes whereas the previous practice used external ones. The general scheme for producing and maintaining these low pressures was to place the liquid benzene in a side limb of the discharge tube, to immerse it in liquid air to freeze the liquid to a solid cake, and then to seal the side limb and evacuate the system with a mercury diffusion pump until the residual air was so attenuated that a discharge could not be produced. The liquid air bath was then partially removed to allow the frozen benzene to warm slightly so that its vapor at low pressure could continuously diffuse through the discharge tube to a liquid air trap where it was condensed. In this manner equilibrium between speed of pumping and rate of sublimation was soon established and could be modified to give pressures between the limits of 0.01 and 0.10 mm. This method of maintaining a constant flow of vapor in the tube helped to remove any decomposition products as soon as they were formed and in conjunction with the low kinetic energy, and consequent small molecular disruptive power of the Tesla discharge gave some assurance that the spectrum originated in the benzene molecule. As a further precaution against contamination a new tube and liquid air trap were used for each exposure.

The first attempt to obtain the desired spectrum was made with the so-called "electrodeless" discharge, produced by placing the discharge tube in a helix of stout brass rod through which the current from a 1 KW Thordarson transformer was passed. A few trials sufficed to show that the spectrum obtained under these conditions was not that of the undecomposed molecule, but was due apparently to molecular fragments. Moreover, this discharge was very sensitive to slight fluctuations in pressure; with the pressure above a certain limiting value the free electrons and ions did not seem to attain a velocity sufficiently high to excite the rest of the vapor; with pressures too low the intensity of the glow suffered appreciably. At times this discharge showed a tendency to form a shell adjacent to the inside wall of the tube which electrically shielded the interior and caused a luminescent cylinder to form; the dark core of this cylinder rendered the discharge quite unsuitable for photographing.

It is interesting to note that the exciting coil and discharge tube grew quite warm during the passage of the current through the former; at the end of a run the latter invariably cracked, the cracks following the helix around the tube; whether the rupture of the glass was caused by thermal or electrical strain was not determined.

The next attempt was made with electrodes of lead foil wrapped around a Pyrex tube. This set-up yielded a satisfactory spectrum but endless trouble

was experienced with the breakdown of the glass along the surface between the electrodes. The presence of air streaks in the glass made trouble certain.

Finally it was decided to install internal electrodes, a procedure which had hitherto been regarded as hazardous because of the possibility of excessive decomposition of the vapor. Such electrodes, however, proved the

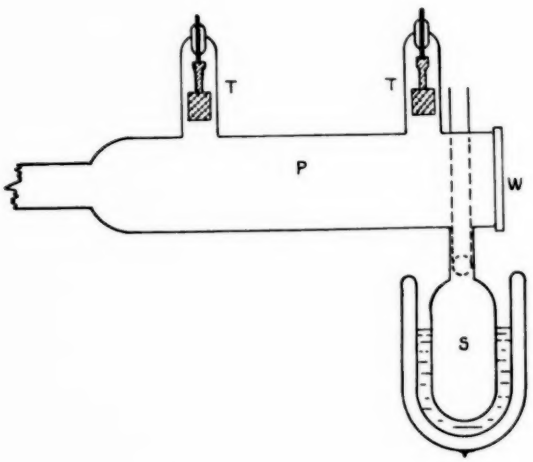


Fig. 1. Discharge tube.

most satisfactory of all the arrangements tried and in most cases caused no greater decomposition than the other types. This system was used to obtain all the results herein reported. Fig. 1 shows the discharge tube which consisted of a cylinder of Pyrex, *P*, with a quartz window, *W*, sealed on at one end with de Khotinsky cement; the other end was connected to a vacuum

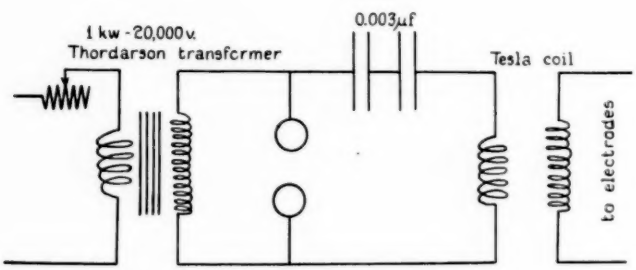


Fig. 2. Electrical connections.

system and a mercury diffusion pump. The electrodes, *T*, were cylinders of aluminum attached to tungsten seals; a side bulb, *S*, held the benzene.

The electrical system is shown in Fig. 2. When properly tuned this circuit gave a potential of about 120,000 volts as estimated from the spark produced between metal points.

Spectroscopic and Photographic Methods

In this work two spectrographs were employed:

(a) A Hilger size C quartz spectrograph, giving a photograph 200 mm in length for the range 2100A to 7000A. On this instrument exposures ranging from 3 to 12 hours were made; a plate exposed for 12 hours was used for the final measurements. For comparison, the spectrum of a mercury arc was superposed on the middle of the benzene spectrum with the aid of a reducing stop on the slit.

(b) A Hilger E_1 quartz spectrograph (Littrow mounting) giving a spectrum 140 mm in length for the region 2500A to 3000A. The spectrum of the mercury arc was superposed on these plates as on the others.

All photographs were taken on Eastman 33 plates of a special thin glass so that they could conform to the curvature of the plate holder without danger of breaking. In the earlier stages of the work Nujol and transformer oil were tried as sensitizers but were later discarded since they did not appreciably enhance the intensities of the ultra violet lines and were not deemed of sufficient value to warrant the extra trouble.

The spectra obtained with the smaller instrument extended almost 150A farther into the ultra-violet than those from the larger one; on the latter no bands were measured beyond 2600A while on the former they were recorded as far as 2471A. This difference is probably due to the greater absorption of the thicker quartz prism in the big spectrograph. On the other hand the large Hilger resolved some of the bands and permitted greater accuracy in measurement; hence, to obtain a complete spectrum of considerable accuracy the data obtained with the two instruments have been combined.

Wave-length Measurements

All plates were measured on a Société Genevoise ruling engine whose ruling mechanism had been replaced by a plate holder and a fixed telescope with cross hair attachment. The screw head was graduated in divisions of 0.005 mm with a vernier which allowed readings to be made to 0.001 mm. Tests on the accuracy of the screw showed that any deviations or flaws in it were negligible compared to other errors. The wave-lengths of the unknown lines were calculated by means of the parabolic interpolation formula:

$$\lambda_i = \lambda_0 + a s_i + b s_i^2$$

where λ_0, a and b are constants determined from the mercury lines[2] and s_i is the reading of the measuring engine corresponding to the i^{th} line. This formula proved to be as accurate as the observations for ranges of 200A in the lower visible and ultra-violet and involved much less labor than the Hartmann formula. The whole spectrum was covered in overlapping sections of 200A.

Each plate was measured in the center of the spectrum to avoid any error due to curvature of the lines. The further precaution was taken of having

[2] Kayser, Tabelle der Hauptlinien der Linienspektra J. Springer, Berlin 1926.

TABLE I.

λ in A A & B	1/λ in cm^{-1} A & B	1/λ in mm^{-1} McV., M. & S.	λ in A A & B	1/λ in cm^{-1} A & B	1/λ in mm^{-1} McV., M. & S.
2471.1*	40456		2777.2	35996	
2483.0*	40262		2789.4	35839	3586
2528.5*	39537		2800.2	35701	3570
2541.5*	39335		2810.6	35569	
2547.3*	39245		2812.3	35535	3554
2551.6*	39179		2815.2	35511	
2562.5*	39013		2817.2	35485	
2571.9*	38870		2820.0	35450	
2585.1*	38672		2822.6	35417	3542
2589.0*	38613		2824.7	35391	3537
2595.0*	38524		2828.1	35349	
2599.9*	38452		2830.2	35322	
2602.6	38411		2832.9	35289	3528
2608.7	38321		2834.5	35269	
2613.6	38250		2835.7	35254	
2619.8	38159		2837.9	35227	3521
2624.8	38086		2841.0	35188	
2629.8*	38014		2848.6	35094	3512
2631.1*	37996		2852.9	35041	3504
2641.7*	37843		2854.4	35023	
2647.8*	37776		2857.5	34985	3498
2649.0*	37739		2866.5	34875	
2657.5	37618	3765	2895.5	34526	3454
2663.6	37532	3752	2898.1	34496	
2667.4	37478		2900.6	34465	3445
2667.9	37472		2903.7	34428	
2668.4	37465		2909.1	34364	3438
2669.1	37455		2911.9	34331	
2673.5	37393	3741	2914.5	34301	
2678.6	37321		2917.6	34264	3428
2684.6	37233		2920.5	34230	3422
2685.6	37224	3725	2922.8	34203	
2689.2*	37175	3717	2925.5	34172	
2690.2	37061		2930.4	34115	3411
2696.2	37078	3708	2932.9	34086	
2701.7	37002	3703	2937.0	34038	3405
2702.2	36995		2951.0	33876	3390
2705.1*	36956		2961.0	33763	3376
2707.7*	36921	3693	2980.6	33540	3357
2714.0*	36835	3686	2983.5	33507	
2718.6*	36773		2985.9	33481	
2727.8	36648	3666	2989.5	33440	
2729.6	36624		2995.1	33378	3339
2734.6	36557		2998.5	33340	
2736.5	36532		3003.4*	33286	
2739.1	36497	3652	3009.5	33218	3322
2740.5	36478		3012.8*	33182	
2743.7	36436		3018.6*	33118	3308
2745.4	36413	3642	3052.7*	32748	
2747.3	36388	3636	3060.6*	32664	
2751.2	36337		3068.3*	32582	3257
2752.7	36317		3074.2	32519	
2755.9	36275		3075.5*	32506	
2757.7	36251	3625	3080.1	32457	3242
2759.6	36239		3085.6	32399	
2763.4	36176		3090.4*	32349	
2764.9	36157	3611	3095.1*	32300	
2771.7	36068		3102.0*	32228	3229
2775.4	36020	3602	3158.1	31654	

each of us independently measure each plate twice, once when it was run along the measuring engine forward and once backward; in this way each line was approached from both sides. The agreement obtained in these sets of observations was most satisfactory, the difference rarely exceeding ± 0.5A and in most cases being less than ± 0.25A. The four measurements of each line have been averaged and converted to wave numbers in vacuo.

Preparation of Benzene

Merck's product was shaken six times with concentrated sulfuric acid; at the end of this treatment no color was imparted to fresh acid. The benzene was then washed successively with concentrated sodium hydroxide, dilute sodium hydroxide, and distilled water, until the final wash water was neutral to litmus. The resulting product was dried over sodium for 25 hours and redistilled from the same. A large fraction came over at a constant temperature and this was taken for use. B. P. 80.0°C at 760 mm Hg pressure.

Results

The general scheme of the bands is shown in the photograph, Fig. 3. The following table gives the average results obtained from the two spectrographs. Lines observed only on the smaller spectrograph are marked with an asterisk. The results of McVicker, Marsh, and Stewart are given for comparison.

While a rough notion of the relative intensities of the bands may be gathered from Fig. 3, a more exact measure for the most prominent band groups is given in the microphotograph, Fig. 4. This was made on a Koch-Goos microphotometer from a plate taken on the large spectrograph. The ratio of length on this curve to length on the plate is 2:1.

It was found that all the principal bands could be accounted for with an accuracy of ± 3 cm^{-1} by the following equations:

$$1/\lambda = 37485 + 924m - 161n \qquad 1/\lambda = 37425 - 986m - 162n$$

$$1/\lambda = 37398 + 924m - 161n \qquad 1/\lambda = 36479 - 991m - 162n$$

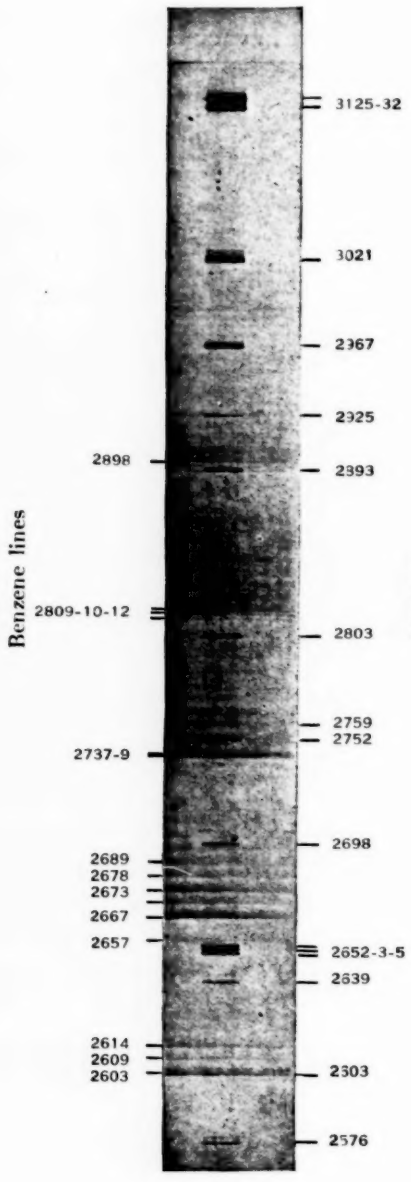
$$1/\lambda = 37485 - 986m - 162n \qquad 1/\lambda = 36412 - 991m - 162n$$

where m and n are assigned integral values. In one band (2667.4) some of the fine structure was observed, the wave-length difference being about ± 0.5A. This agrees with the value reported by Henri[3] in the absorption spectrum. It is interesting to note in this connection that the wave-number differences 991 and 162 cm^{-1} appearing in these equations are found also in the Raman spectrum of benzene. It is hoped that before long some definite significance can be attached to these values.

It may be well to review the evidence supporting the assumption that this spectrum originates in the benzene molecule for in spite of all precautions some decomposition did occur. At the end of the 12 hour runs the surfaces of

[3] Henri, Structure des Molecules, Paris, 1925, p. 109.

the aluminum electrodes were found to be covered with a layer of carbon and the discharge tube showed a very thin film of a shellac-like substance adher-



Hg lines Fig. 3.

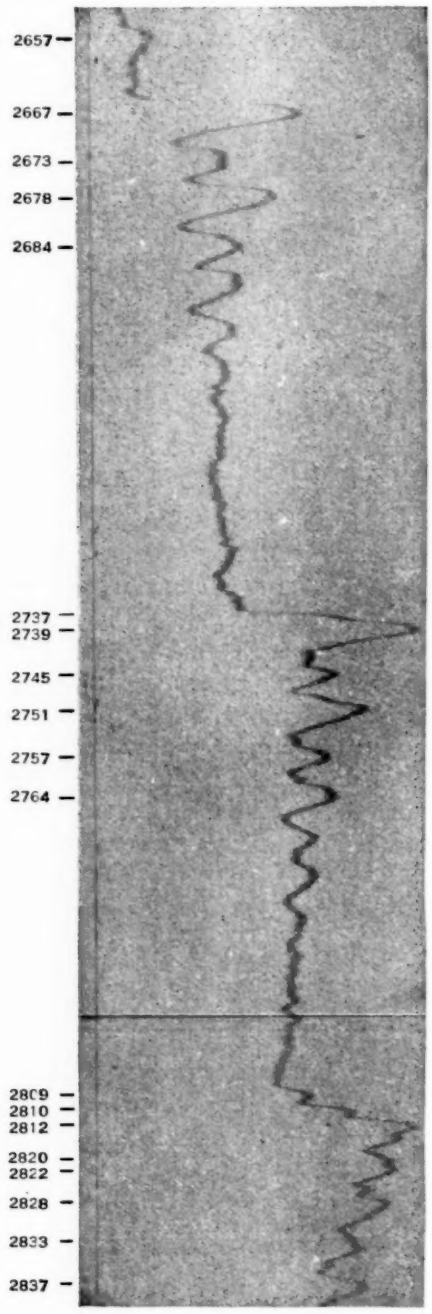


Fig. 4.

ing to the walls. However, despite the appearance of these products there is little doubt that the spectrum observed is actually that of benzene. Apart

from the fact that the decomposition products seem non volatile, the following considerations point to the same conclusion.

First, it was observed that conditions which produced the greatest visible decomposition gave spectra of low intensity. Thus, for example, as the pressure is lowered decomposition is decreased while the intensity of the glow is increased. This is just what is to be expected since, for a given energy input, the larger the amount of energy used in molecular rearrangements, the smaller will be the fraction of the total energy as light.

Second, the regularity exhibited by the spectrum seems to militate against any decomposition hypothesis, for this regularity implies a uniformity in the system which produces it; if this system is a benzenoid molecule, its symmetry is easily understood, but if it is produced by some dissociation or rearrangement under the stress of the discharge then it is necessary to postulate an absolute uniformity of decomposition which would be hard to concede from a theoretical view point and would certainly not account for the fact that several decomposition products are actually found.

Aside from these considerations, which involve only the emission spectra, the results can be checked with the spectra in solution. For instance, Dickson[4] has observed the fluorescence spectrum of benzene in alcohol solution. It is well known that a solvent shifts the spectrum of a substance in solution but this shift is generally a translation of the system as a whole so that the relative positions of the bands remain unchanged. It is found that if 19 units of wave-number are added to the values given by Dickson the broad bands of his spectrum coincide with the principal emission bands which we have observed.

Even more convincing is the agreement between the absorption and emission spectra of the vapor, which prove to have identical band arrangements. The emission spectrum should include the bands found in absorption but the far ultra-violet part of the former is lacking due to the absorption by unexcited benzene molecules in the discharge tube. However, it is found that the most refrangible emission band group coincides with the bands of the red end of the absorption spectrum as determined by Henri.[5] This arrangement is shown in the following table.

TABLE II.

Absorption Bands of benzene vapor after Henri λ	Emission Bands of benzene vapor (A & B) λ	Absorption Bands of benzene vapor after Henri λ	Emission Bands of benzene vapor (A & B) λ
2528.6	2528.6	2599.9	2599.7
2541.7	2541.5	2603.0	2602.6
2552.5	2551.7	2610.2	2610.1
2589.0	2588.7	2613.9	2613.5
2595.2	2595.2		

[4] Dickson, Zeit. Wiss. Photo. **10,** 166 (1912).

[5] Henri, J. de Phys. et Rad. **3,** 181 (1922).

This check is sufficient to establish the fact that the carrying structure is the the same, and, since no decomposition is to be expected, nor indeed is any found, in the absorption work, it follows that both spectra are due to undecomposed benzene.

The foregoing considerations, in addition to demonstrating that the benzene molecule is the carrier of the spectrum, also indicate a very satisfactory agreement between our work and the known absorption and fluorescence spectra. It may be of interest to conclude with a comparison of our results with those of McVicker, Marsh and Stewart. Taking the results from both spectrographs we have recorded the wave-length of about 110 bands and in addition to more than doubling the known number of emission bands have given evidence of two new band systems in the far ultra-violet. We do not claim to have measured all the bands in the spectrum, however, for in many cases bands could be seen on the plates with the naked eye which were not susceptible of measurement under the microscope. We have also shown that many of the lines reported by McVicker, Marsh, and Stewart are really doublets. A number of our measurements when expressed in wave numbers seem to be about 30 units smaller than those of the corresponding lines in the work of McVicker, Marsh, and Stewart. This is interesting on account of the fact that in the comparison made between their results and Hartley's values for the absorption of benzene approximately 20 units were added to the latter in order to make the regularities coincide.

In conclusion the authors wish to express their thanks to Dr. John Johnston at whose suggestion the work was undertaken, to Dr. A. E. Ruark who gave valuable assistance with the experimental work, to Professor Uhler for much help in the spectroscopic and photographic work and for suggesting the methods of measurement and calculation, to Professor McKeehan who kindly placed the resources of the Sloane Physics Laboratory at our disposal. The authors wish also to thank the Commonwealth Fund for the fellowship which one of them held and without which he would have been unable to undertake this research.

NOTE ON THE THEORY OF THE INTERACTION OF FIELD AND MATTER

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(Received November 12, 1929)

Abstract

The paper develops a method for the systematic integration of the relativistic wave equations for the coupling of electrons and protons with each other and with the electromagnetic field. It is shown that, when the velocity of light is made infinite, these equations reduce to the Schroedinger equation in configuration space for the many body problem. It is further shown that it is impossible on the present theory to eliminate the interaction of a charge with its own field, and that the theory leads to false predictions when it is applied to compute the energy levels and the frequency of the absorption and emission lines of an atom.

THE relativistic theory of the interaction of electrons and protons with each other and with the electromagnetic field has been developed in two papers.[1] The theory is developed in close analogy to the corresponding classical theory: the field is on the one hand determined by the configuration of the charges; and the motion of the charges is affected by the field. The interaction between two charges is not then, on this theory, expressed directly as a function of the configuration of the charges, but as the effect on each of the charges of the field induced by the other. On the classical theory this procedure involves grave difficulties, because each charge reacts also with its own field. The proper energy of this interaction is, for point charges infinite; and it depends upon the motion of the charge. On the classical theory one tried to avoid this difficulty by ascribing to the elementary charges a finite size; but it was not possible to carry through the theory in a way that was not completely arbitrary; nor was it possible to make the work relativistically invariant. One of the purposes of the present paper is to see in how far these difficulties persist in the quantum theory, and in what measure they render impossible the application of the theory.

We may recapitulate briefly the main points of divergence between the present quantum theoretic treatment and the classical theory. In the first place the state of the matter is here represented, not by a trajectory, but by a wave function. Further, the Hamiltonian for the matter is that derived from Dirac's linear wave equation, and not from the quadratic wave equation which would follow from the classical relativistic Hamiltonian. Finally, both the material waves and the electromagnetic waves are quantized, the matter

[1] W. Heisenberg and W. Pauli, Zeits. f. Physik **56**, 1 (1929); ibid. in press. The second of these two papers is referred to in this work as LC. I am greatly indebted to Professor Heisenberg and Professor Pauli, not only for the opportunity of seeing their work before its publication, but also for their very valuable criticism and advice.

to make the particles satisfy the exclusion principle, the field to make the quanta satisfy the Einstein-Bose statistics. This precedure leads to a formal difficulty; for the fourth Maxwell equation

$$\text{div } \boldsymbol{E} - 4\pi\rho = 0 \tag{1}$$

is inconsistent with the quantum conditions, according to which there are functions of the electromagnetic potentials which do not commute with div $\boldsymbol{E}$ but which must commute with the charge density. The two papers of Heisenberg and Pauli are distinguished chiefly by different methods of resolving this difficulty. In the former paper new terms were added to the fourth Maxwell equation to make the new equation consistent with the quantum conditions; in obtaining physical results these terms were to be made to vanish. In the second paper a much more satisfactory method has been used, which takes advantage of the fact that the left hand side of (1) is a constant of the motion for all systems involving matter and radiation; and it is shown that this constancy follows from the gauge invariance of the Hamiltonian for all such systems. The solution of the dynamical problem thus reduces to finding a wave function for the coupled system of field and matter, which makes the Hamiltonian for the coupled system a diagonal matrix, and which in addition makes the left hand side of (1) vanish. The wave function has thus to satisfy not only the Hamiltonian wave equation, but also a series of wave equations which express the fact that (1) is satisfied at all points in space. It is from this set of wave equations that we shall start in this paper; we shall write them first in the form given in LC Eq. (68), in which the wave function is taken as a function of the Cartesian coordinates

$$\boldsymbol{q}_P = (q_P^{(1)}, q_P^{(2)}, q_P^{(3)}) \; ; \; P = 1, 2, \cdots, N$$

and spin variables

$$\sigma_P \; ; \; P = 1, 2, \cdots, N$$

of the N particles in the system, the number of quanta

$$M_{r\lambda}$$

of frequency

$$\nu_r$$

vector of propagation $\boldsymbol{K}_r = (K_r^1, K_r^2, K_r^3)$; $K_r = \nu_r/c$ and polarization λ, and finally a third set of variables P_{r3}, which are essentially the constant components of the electric field parallel to the vectors of propagation $\boldsymbol{K}_r$. We shall first show that it is possible to eliminate the P_{r3}'s from the wave equations in such a way that (1) is automatically satisfied. The reason why this is possible is that the condition (1) determines div $\boldsymbol{E}$ precisely—instead of determining only the relative probabilities of different values of div $\boldsymbol{E}$,—when the configuration of the charges is known, so that the values of the P's so determined can be put at once into the Hamiltonian. When this is done the variables Q_{r3} canonically conjugate to the P's must disappear from the Hamiltonian, since otherwise the Hamiltonian would not be consistent with (1);

we shall show that this is in fact the case, and then proceed to an investigation of the resulting Hamiltonian.

It should be observed that the wave functions must satisfy, in addition to the wave equations in configuration space, the condition that they be antisymmetric in all the electrons of the system, and antisymmetric in all the protons of the system. Only wave functions satisfying these conditions are to be considered in this paper; and it will therefore be unnecessary to indicate the antisymmetry of the wave functions explicitly. The fact that electrons and protons satisfy the exclusion principle is largely irrelevant to the difficulties discussed in this work;for these difficulties persist even in the one-electron problem. On the other hand it is to be hoped that the resolution of the errors in the present theory will make the heuristic postulate of the exclusion principle unnecessary.

We shall look for a solution of the wave equation in which both wave function and characteristic values are expanded in powers of v/c. It has already been shown by Breit[2] that, when the interaction of the particles may be treated as small, and radiation processes may be neglected, that these interaction terms give a contribution to the energy of the system, which, in second order in v/c, agrees with that computed from Breit's equation.[3] We shall not retain the assumption that the interaction terms are small, and shall show, somewhat more generally, that when the proper energy terms are systematically neglected, the characteristic energy levels and the wave function are determined by Breit's equation. This equation is, of course, not relativistically invariant; and it takes no account of radiation processes. In order to remedy these defects one must retain the proper energy terms; and we shall show that it is then possible to make a *formally* satisfactory theory to give the shape and position of all spectral lines, and the energy of the normal state. The theory, is, however, wrong, since it gives a displacement of the spectral lines from the frequency predicted on the basis of the nonrelativistic theory which is in general infinite. This displacement arises from the infinite interaction of the electron with itself; this interaction depends upon the state of the material system; and the difference in the energy for two different states is not in general finite. Thus the present theory gives no more than the nonrelativisitic theory of Jordan, Klein and Wigner.[4] It seems improbable that Breit's equation gives the energy levels of an atom correct to second order terms in v/c; but we shall see that there is ground for supposing that it does give the separation of the fine structure levels correctly in this order. On the other hand the displacement in the frequency of the spectral lines which arises from the proper energy should be of the second order in v/c, and is thus larger than the natural line breadth, which is of the third order; and on the present theory it is not possible to compute this displacement. We shall return later to a consideration of these difficulties.

[2] G. Breit, Phys. Rev. **34,** 553 (1929).

[3] Breit, ibid., Eq. (6).

[4] P. Jordan and O. Klein, Zeits. f. Physik **45,** 751 (1927). P. Jordan and E. Wigner, ibid. **47,** 631 (1928).

1. The condition that the left hand side of (1), regarded as an operator on the wave function ψ of the variables

$$q_P, \sigma_P, M_{r\lambda}, P_{r3}$$

shall make the wave function vanish at every point in space, gives a series of wave equations

$$I \qquad C_r\Psi = \left[P_{r3} + \sum_P e_l v^{r0}(q_P) \right] \psi(q_P, \sigma_P, M_{r\lambda}, P_{r3}) = 0$$

which must hold for all values of the K_r consistent with the boundary conditions. Here the v^{ro} are functions defined in LC (54):

$$v^{r0}(q_P) = \frac{2}{\pi}(ck_r{}^3L^3)^{-1/2} \sin \pi k_r{}^{(1)} q_P{}^{(1)} \sin \pi k_r{}^{(2)} q_P{}^{(2)} \sin \pi k_r{}^{(3)} q_P{}^{(3)} \qquad (2)$$

Here L is the length of the fundamental cube, or Hohlraum, and is taken finite in LC to avoid the introduction of a continuous manifold of normal coordinates; in all our results we shall make L become infinite. Furthermore the Hamiltonian for the coupled system, regarded as an operator on the same wave function, gives the wave equation

$$\begin{aligned} II \qquad & \left\{ -E + \sum_r \left[\sum_{\lambda=1,2} M_{r\lambda} h\nu_r + \pi \nu_r P_{r3}{}^2 \right] + \sum_{P=1}^{N} \left[\frac{hc}{2\pi i}(\alpha^P \operatorname{grad}_P) + m_P \alpha_0{}^P c^2 \right] \right\} \psi \\ & + \left\{ \sum_{P=1}^{N} [e_P A_0{}^0(q_P) + e_P(\alpha^P \cdot A^0(q_P))] \right\} \psi \\ & + \left\{ i \sum_r \sum_{\lambda=1,2} \sum_{P=1}^{N} \mu_P{}^{r\lambda} [(M_{r\lambda}+1)^{1/2} \Delta_{r\lambda}{}^{-1} - M_{r\lambda}{}^{1/2} \Delta_{r\lambda}] \right\} \psi \\ & + \left\{ \sum_r \sum_{P=1}^{N} \mu_P{}^{r3} Q_{r3} \right\} \psi = (+H - E)\psi = 0. \end{aligned}$$

Here $A_0{}^0$ is the external scalar potential, and A^0 the external vector potential; and $\Delta_{r\lambda}$ is an operator which transforms $M_{r\lambda}$ into $M_{r\lambda} - 1$, and leaves all other variables unchanged; the α^p's are operators which operate only on σ_p, and are derived from the Dirac matrices $\alpha_{\rho\sigma}{}^l$ by the definition

$$\alpha_l{}^P F(\sigma_P) = \sum_{\rho_P} \alpha_{\sigma_P}{}^l{}_{\rho_P} F(\rho_P) \; ; \quad \alpha_0{}^P F(\sigma_P) = \sum_{\rho_P} \alpha_{\sigma_P}{}^0{}_{\rho_P} F(\rho_P).$$

Further the Q_{r3} are canonically conjugate to the P_{r3} so that

$$[P_{r3} Q_{r'3}] = \frac{h}{2\pi i} \delta_{rr'} \qquad (3)$$

Finally the functions $\mu_p{}^{r\lambda}$, $\mu_p{}^{r3}$ are defined in LC (59):

$$\mu_P{}^{r3} = e_P c \left(\frac{\nu_r}{2} \right)^{1/2} \sum_{l=1}^{3} \alpha_l{}^P v_l{}^{r3}(q_P)$$

$$\mu_P{}^{r\lambda} = e_P c \left(\frac{h}{2\pi\nu_r}\right)^{1/2} \sum_{l=1}^{3} \alpha_l{}^P v_l{}^{r\lambda}(q_P) \; ; \; \lambda = 1,2 \tag{4}$$

$$v_l{}^{r\lambda}(q_P) = \left(\frac{8}{L^3}\right)^{1/2} F^r_{l\lambda} \cos \pi k_l q_P{}^{(l)} \sin \pi k_{l'} q_P{}^{(l')} \sin \pi k_{l''} q_P{}^{(l'')} \; ;$$

$$l = 1,2,3.$$

$$\lambda = 1,2,3.$$

The square matrix $F^r_{l\lambda}$ is given by the scheme

l \ $\lambda=$	1	2	3
1	$\epsilon_2{}^r/(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}$	$\epsilon_1\epsilon_3/(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}$	ϵ_1
2	$-\epsilon_1/(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}$	$\epsilon_2\epsilon_3/(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}$	ϵ_2
3	0	$-(\epsilon_1{}^2+\epsilon_2{}^2)^{1/2}$	ϵ_3

(5)

where the $\epsilon_l{}^r$'s are the direction cosines of the vector $\boldsymbol{K}_r$. It should be observed that

$$\frac{hc}{2\pi i}(\mathbf{a}^P \quad \mathrm{grad}_P) e_P v^{r0}(q_P) = \frac{h}{2\pi i} \mu_P{}^{r3}. \tag{6}$$

This equation, together with (3), shows that

$$[HC_r] = 0 \tag{7}$$

for all r, so that all the C_r's are constants of the motion. The equations I and II are those given[5] in LC (68).

From I we see that the wave function must be singular in the P's. We may avoid the use of singular functions by making a contact transformation from the variables P to Q, and writing the wave function as:

$$\psi(q_P, \sigma_P, M_{r\lambda}, Q_{r3}).$$

For we may then solve (3) by taking

$$P_{r3} = \frac{h}{2\pi i} \frac{\partial}{\partial Q_{r3}}.$$

If now we set

$$\psi(q_P, \sigma_P, M_{r\lambda}, Q_{r3}) = e^{-2\pi i/h \sum_r \sum_p e_p v^{r0}(q_p) Q_{r3}} \phi\,(q_P, \sigma_P, M_{r\lambda}, Q_{r3}) \tag{8}$$

the equations I give us

$$\frac{\partial \phi}{\partial Q_{r3}} = 0 \tag{9}$$

for all r so that

$$\phi = \phi(q_P, \sigma_P, M_{r\lambda}).$$

[5] In LC (68) the A's are dropped.

Further the Hamiltonian II becomes

$$
\begin{aligned}
e^{-2\pi i/h}\sum_r \sum_P e_P v^{r0}(q_P)Q_{r3}\Big\{ & -E+\sum_r\Big[\sum_{\lambda=1,2}M_{r\lambda}h\nu_r+\pi\nu_r\sum_{P,P'}^{N}e_Pe_{P'}v_0{}^{r0}(q_P)v^{r0}(q_{P'})\Big] \\
& +ih\sum_r\sum_P\nu_re_Pv^{r0}(q_P)\frac{\partial}{\partial Q_{r3}}-\frac{h^2}{4\pi}\sum_r\nu_r\frac{\partial^2}{\partial Q_{r3}}+\sum_P\Big[\frac{hc}{2\pi i}(\boldsymbol{\alpha}^P\mathrm{grad}_P)+m_Pc^2\alpha_0{}^P\Big] \\
& -c\sum_r\sum_P e_P(\boldsymbol{\alpha}^P\ \mathrm{grad}_P)v^{r0}(q_P)Q_{r3}+\sum_P e_P[A_0{}^0(q_P)+(\boldsymbol{\alpha}^P\cdot\boldsymbol{A}^0(q_P))] \qquad (10)\\
& +\sum_r\sum_P\mu_P{}^{r3}Q_{r3}+i\sum_r\sum_{\lambda=1,2}\sum_P\mu_P{}^{r\lambda}[(M_{r\lambda}+1)^{1/2}\Delta_{r\lambda}{}^{-1} \\
& -M_{r\lambda}{}^{1/2}\Delta_{r\lambda}]\Big\}\phi(q_P\sigma_PM_r)=0.
\end{aligned}
$$

The terms in Q drop out because of (6); the terms in $\partial/\partial Q$ give nothing because of (9). The equations I and II thus reduce to the single system

$$
\begin{aligned}
&\Big\{-E+H_0+\sum_{r\lambda}M_{r\lambda}h\nu_r+i\sum_{r\lambda P}\mu^{r\lambda}[(M_{r\lambda}+1)^{1/2}\Delta_{r\lambda}{}^{-1}-M_{r\lambda}{}^{1/2}\Delta_{r\lambda}]\Big\}\phi=0 \qquad (11)\\
&H_0=\sum_P\Big\{\frac{hc}{2\pi i}(\boldsymbol{\alpha}^P\ \mathrm{grad}_P)+m_Pc^2\alpha_0{}^P+\rho_P[A_0{}^0(q_P)+(\boldsymbol{\alpha}^P\cdot\boldsymbol{A}^0(q_P))]\Big] \\
&\qquad\qquad +\pi\sum_{P'}\sum_r e_Pe_{P'}\nu_rv^{r0}(q_P)v^{r0}(q_{P'})\Big\}.
\end{aligned}
$$

It is this system which we must now investigate.

The terms

$$G(q_P,q_{P'})=\sum_r\pi\nu_rv^{r0}(q_P)v^{r0}(q_{P'})$$

may readily be evaluated,[6] and give for $L\to\infty$

$$G(q_P,q_{P'})\to-\frac{1}{2r_{PP'}}\ ;\ r_{PP'}=|\,\boldsymbol{q}_P-\boldsymbol{q}_{P'}\,|\ . \qquad (12)$$

The terms for p and p' different give the electrostatic interaction of the two particles; the terms for $p=p'$ give the infinite electrostatic proper energy of the particles; on the present theory it is not possible, as it was on the non-relativistic theory,[4] to eliminate these terms; the physical ground for this impossibility has already been indicated, and lies in the fact that the field acting on any particle is the sum of the fields induced by all particles; it is a consequence of the principle of superposition for the field. These electrostatic proper energy terms do not, however, interfere with the application of the theory, since they are constants, and may be dropped from (11) without altering the form of the wave function. We shall find other infinite proper

[6] W. Heisenberg and W. Pauli, Zeits. f. Physik **56**, 1 (1929). Eq. (115); G. Breit, reference 2 Eq. (57). Breit has independently evaluated the P_{r3} terms in the Hamiltonian; and I am much intebted to him for informing me of his result.

energy terms in the course of the work; but these will turn out not to be constants, but to depend upon the configuration of the system; dropping them does alter the form of the wave function.

If we now neglect the coupling between matter and the light quantum field the wave equation reduces to

$$\left[-E+H_0+\sum_{r\lambda} M_{r\lambda}h\nu_r\right]\phi=0 \tag{13}$$

and for the case that no quanta are present we have

$$\left\{-E+\sum_P\left[\frac{hc}{2\pi i}(\boldsymbol{\alpha}^P\cdot\operatorname{grad}_P)+m_Pc^2\alpha_0{}^P+e_P[A_0{}^0(q_P)+(\boldsymbol{\alpha}^P\cdot\boldsymbol{A}(q_P)]\right]\right.$$
$$\left.-\sum_{PP'}\frac{e_Pe_P{}'}{2r_{PP'}}\right\}\phi(\sigma_P,q_P)=0. \tag{14}$$

We shall show that the terms which we have neglected in (12) are small of the order $(v/c)^2$; and by neglecting other terms of the same order, (13) can be considerably simplified. For consider first the equation

$$\left\{-E+\sum_P\left[\frac{hc}{2\pi i}(\boldsymbol{\alpha}^P\cdot\operatorname{grad}_P)+m_Pc^2\alpha_0{}^P\right]\right\}\phi=0. \tag{15}$$

For N-free uncoupled particles. If we choose all matrices$\| \alpha_{\rho_p}{}^{l}{}_{\sigma_{p'}}\|$ of the form

$$\begin{pmatrix} 0 & 0 & b & a \\ 0 & 0 & c & d \\ \bar{b} & \bar{c} & 0 & 0 \\ \bar{a} & \bar{d} & 0 & 0 \end{pmatrix} \tag{16}$$

and all the $\|\alpha_{\rho_p}{}^{o}{}_{\sigma_p}\|$ of the form:

$$\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{16}$$

and satisfying of course

$$[\alpha^{\mu,P}\alpha^{\nu,P'}]=0 \text{ for } P\neq P' \; ; \; [\alpha^{\mu,P}\alpha^{\nu,P}]^+=2\delta\mu\nu \tag{17}$$

then any $\phi(\sigma_p)$ in which n of the σ_p's have either of the values 3 or 4 will be small compared with any of the ϕ's for which all of the σ_p's have the values 1 or 2 of the order $(v/c)^n$. Now the terms

$$-\sum_{PP}{}'\frac{e_Pe_{P'}}{2r_{PP'}}, \quad e_PA_0{}^0(q_P)$$

in (14) do not involve the α^p's, while the terms

$$e_P(\boldsymbol{\alpha}^P\cdot\boldsymbol{A}(q_P))$$

are small of the order v/c; thus as v/c is made to vanish, all the solutions of (14) vanish except those for which all the σ_p's have the values 1 or 2; and (14) reduces to

$$\left[-E+\sum_P\left\{m_Pc^2+e_PA_0{}^0(q_P)-\frac{h^2}{8\pi^2m_P}\Delta_P-\sum_{P'}{}'\frac{e_Pe_{P'}}{2r_{PP'}}\right\}\right]\phi(\sigma_Pq_P)=0 \quad (18)$$

for all σ_p's $=1$ or 2 and

$$\phi(\sigma_Pq_P)=0 \text{ for any } \sigma_P=3 \text{ or } 4$$

which is the Schroedinger equation for the N-body problem.[7] It would thus be possible to take (18) as the starting point for our systematic solution of (11) in powers of v/c. We shall not do this, however, as it would complicate the analysis, and lead to no new results. We shall thus give up the assumption that the α's are written in the form (16), and take for our zero'th approximation to (11), the solutions of (14).*

2. We may write the equations (11) *seriatim*:

$$\sum_{r\lambda}M_{r\lambda}=M=0;(-E+H_0)\phi=-i\sum_{r\lambda P}\mu_P{}^{r\lambda}\phi(1_{r\lambda});\quad \phi=\phi(0_{r\lambda}) \quad (11.1)$$

$$M=1\quad\begin{cases}(-E+h\nu_r+H_0)\phi(1_{r\lambda})=+i\sum_P\mu_P{}^{r\lambda}\phi-\left[i\sum_{r'\lambda'}\sum_P\mu_P{}^{r'\lambda'}\phi(1_{r\lambda},1_{r'\lambda'})\right]\\ \quad -2^{1/2}i\sum_P\mu^{r\lambda}\phi(2_{r\lambda})\end{cases} \quad (11.2)$$

$$M=2\quad\begin{cases}(-E+h(\nu_r+\nu_{r'})+H_0)\phi(1_{r\lambda},1_{r'\lambda'})=+i\sum_P[\mu_P{}^{r\lambda}\phi(1_{r'\lambda'})\\ \quad+\mu_P{}^{r'\lambda'}\phi(1_{r\lambda})]-i\sum_{r''\lambda''}{}'\sum_P\mu_P{}^{r''\lambda''}\phi(1_{r\lambda},1_{r'\lambda'},1_{r''\lambda''})\\ \quad-2^{1/2}i\sum_P[\mu_P{}^{r\lambda}\phi(2_{r\lambda},1_{r'\lambda'})+\mu_P{}^{r'\lambda'}\phi(1_{r\lambda},2_{r,\lambda'})]\end{cases} \quad (11.3)$$

$$\begin{cases}(-E+2h\nu_r+H_0)\phi(2_{r\lambda})=+2^{1/2}i\sum_P\mu_P{}^{r\lambda}\phi(1_{r\lambda})\\ \quad-i\sum_{r'\lambda'}{}'\sum_P\mu_P{}^{r'\lambda'}\phi(2_{r\lambda},1_{r'\lambda'})-3^{1/2}i\sum_P\mu_P{}^{r\lambda}\phi(3_{r\lambda})\end{cases} \quad (11.4)$$

etc.

Now for fixed r, and fixed $\boldsymbol{K}_r$,

$$\mu_P{}^{r\lambda}=0(c^{-1/2})$$

whereas

$$\nu_r=0(c).$$

[7] It is possible to write the two component wave equation when the magnetic interactions are retained up to the order $(v/c)^2$, as has been shown by Breit, reference 2.

* We shall not make explicit use of the fact that the α's are in the form (16); we shall, however, retain the assumption that the α's are small of the order v/c, to obtain $\mu_P{}^{r\lambda}=0(c^{-1/2})$.

Thus we should expect $\phi(1_{r\lambda})$ to be small of the order $c^{-3/2}$, $\phi(1_{r\lambda}, 1_{r'\lambda'})$ to be of the order c^{-3}, and so on, and we should try to find a solution of (11) of the form

$$\begin{aligned} E &= E^{(0)} + E^{(1)} + E^{(2)} \cdots \\ \phi(M_{r\lambda}) &= \phi^{(0)}(M_{r\lambda}) + \phi^{(1)}(M_{r\lambda}) \cdots \end{aligned} \tag{19}$$

with

$$\begin{aligned} E^{(n)} &= 0(c^{-n}) \\ \phi^{(n)}(M_{r\lambda}) &= 0(c^{-n-3/2M}). \end{aligned}$$

It should be observed that in general there will be certain frequencies for which $\phi(1_{r\lambda})$, $\phi(1_{r\lambda}, 1_{r'\lambda'})$ etc. will not converge uniformly for $c \to \infty$; and that for these frequencies the expansions (19) will be illegitimate. The frequencies for which this convergence is non-uniform are those for which

$$+E - \sum_{r\lambda} M_{r\lambda} h\nu_r$$

is a characteristic value of the homogeneous equations

$$(H_0 - \lambda)\phi = 0. \tag{20}$$

Such frequencies will not occur if (20) has no solutions for $\lambda < E$, i.e. if the material system is in a normal state; but in general the expansions (19) must be modified; we shall return to this modification later, and shall see that it gives a satisfactory theory of the absorption and emission of radiation; but for the present we shall assume that the atom is in a normal state, so that (19) is justified.

On the present theory there is no normal state for the matter, because states of infinite negative energy are possible; one may in fact show that, on the present theory, Dirac jumps to such states from states of positive energy, jumps in which the energy and momentum lost by the matter are taken up by the field, are not only possible, but infinitely probable. But that the theory should predict this is a token of an error in the theory; and since the Dirac jumps do not seem to be *directly* responsible for the difficulties with which we are, in this work, most concerned, we shall for the present neglect them.

We shall first give a complete solution for the case that we drop all proper energy terms, for the case, that is, that in all double sums of the form

$$\sum_{PP'} F(q_P, \sigma_P, q_{P'}, \sigma_{P'})$$

we may set the terms with p equal to p' equal to zero. This solution is not unique beyond terms of the second order in v/c; for in the higher orders it is no longer possible uniquely to separate proper energy and interaction energy. But we may readily obtain a possible solution:

$$\phi(M_{r\lambda}) = \prod_{r\lambda} \left[\frac{-i \sum_P \mu_P{}^{r\lambda}}{h\nu_r} \right]^{M_{r\lambda}} \phi \tag{21}$$

where

$$\left[-E+H_0-\sum_{r\lambda}\sum_{PP'}{}'\frac{\mu_P{}^{r\lambda}\mu_{P'}{}^{r\lambda}}{h\nu_r}\right]\phi=0. \tag{22}$$

For if we put these values, for example, in (11.2) we get

$$\begin{aligned}&+i\sum_P\mu_P{}^{r\lambda}\\ &\overline{\qquad\qquad}\left[-E+H_0-\sum_{r'\lambda'}\sum_{PP'}\frac{\mu_P{}^{r'\lambda'}\mu_{P'}{}^{r'\lambda'}}{h\nu_{r'\lambda'}}+h\nu_r\right]\phi\\ &\qquad+\frac{i}{h\nu_r}\left[H_0,\sum_P\mu_P{}^{r\lambda}\right]\phi=i\sum_P\mu_P{}^{r\lambda}\phi.\end{aligned} \tag{23}$$

Now in

$$\sum_P[H,\mu_P{}^{r\lambda}]=\sum_{PP'}\left[\left(\frac{hc}{2\pi i}(\boldsymbol{\alpha}^P\cdot\operatorname{grad}_P)+m_Pc^2\alpha_0{}^P+e_P(\boldsymbol{\alpha}^P\cdot\boldsymbol{A}(q_P)\right),\mu_{P'}{}^{r\lambda}\right] \tag{24}$$

and in

$$\sum_{PP'}\mu_P{}^{r'\lambda'}\mu_{P'}{}^{r'\lambda'}$$

we may put

$$\sum_{PP'}\rightarrow\sum_{PP'}{}'$$

so that

$$\sum_P[H,\mu_P{}^{r\lambda}]=0 \tag{25}$$

and (11.2) is satisfied. In a similar way it may be shown that all the equations (11) are satisfied.

We may evalute the terms

$$\sum_{r\lambda}\frac{\mu_P{}^{r\lambda}\mu_{P'}{}^{r\lambda}}{h\nu_r}=e_Pe_{P'}\frac{c^2}{2\pi}\sum_{ll'}\alpha_l{}^P\alpha_{l'}{}^{P'}\sum_{r\lambda}\frac{v_l{}^{r\lambda}(q_P)v_{l'}{}^{r\lambda}(q_{P'})}{\nu_r{}^2}$$

in (22) by observing that for $l\neq l'$

$$\sum_{r\lambda}\frac{v_l{}^{r\lambda}(q_P)v_{l'}{}^{r\lambda}(q_{P'})}{\nu_r{}^2}=\frac{\partial}{\partial q^l{}_P{}'}\frac{\partial}{\partial q^{l'}_{P'}}F(q_Pq_{P'})\ ;\ \Delta_PF=\frac{\pi}{c^2r_{PP'}}$$

and

$$\sum_{r\lambda}\frac{v_l{}^{r\lambda}(q_P)v_l{}^{r\lambda}(q_{P'})}{\nu_r{}^2}=\frac{-\pi}{2c^2r_{PP'}}-\frac{\partial^2}{\partial q^l{}_P{}^2}F(q_P,q_{P'})$$

so that

$$\sum_{r\lambda}\frac{\mu_P{}^{r\lambda}\mu_{P'}{}^{r\lambda}}{h\nu_r}=\frac{-e_Pe_{P'}}{4}\left\{\frac{(\boldsymbol{\alpha}^P\cdot\boldsymbol{\alpha}^{P'})}{r_{PP'}}+\frac{(\boldsymbol{\alpha}^P\cdot\boldsymbol{r}_{PP'})(\boldsymbol{\alpha}^{P'}\cdot\boldsymbol{r}_{PP'})}{r^3{}_{PP'}}\right\} \tag{27}$$

This gives for ϕ_0

$$\left\{-E+H_0+\frac{1}{4}\sum_{PP'}{}'\frac{e_Pe_{P'}}{r^3{}_{PP'}}[(\boldsymbol{\alpha}^P\cdot\boldsymbol{\alpha}^{P'})r^2{}_{PP'}+(\boldsymbol{\alpha}^P\cdot\boldsymbol{r}_{PP'})(\boldsymbol{\alpha}^{P'}\cdot\boldsymbol{r}_{PP'})]\right\}\phi=0 \tag{28}$$

This is the equation used by Breit.[3] It is patently not relativistically invariant; this means that the proper energy terms are not invariant, and forces us to

retain these terms, at least in part. Furthermore, we have not, in the deduction of (28), used the fact that the atom is in its normal state; in spite of this there is no sign, in the solution, of processes involving the emission or absorption of radiation; for these processes arise from the interaction of the particles with their own field. We have, therefore, to consider the solution of (11) when the proper energy is not neglected; the retention of these terms will preserve the invariance of the theory, and give us an account of radiation processes, but it leads to results in contradiction with experiment; it makes the validity of (28), even to the second order in v/c, doubtful.

3. We can readily find a solution of the form (19) when E^0 and ϕ^0 correspond to a normal state for the matter; but we cannot find this solution in closed form; nor is there an equation in configuration space, corresponding to (28), for ϕ. If we put (19) in (11.2) etc. we get

$$\phi^{(0)}(1_{r\lambda}) = i \sum_m \frac{b_{0m}^{r\lambda} \phi_m^{(0)}}{h\nu_r + E_m^{(0)} - E_0^{(0)}}\ ; \quad \begin{cases} b_{0m}^{r\lambda} = \sum_P \int \cdots \int dq_1^{(1)} \cdots dq_N^{(3)} \\ \left[\sum_{\sigma' \cdots \sigma N} \bar{\phi}_m^{(0)} \mu_P^{r\lambda} \phi_0^{(0)} \right] \\ (H_0 - E_m^{(0)}) \phi_m^{(0)} = 0 \end{cases} \tag{29}$$

and further

$$\begin{aligned} \phi^{(0)}(1_{r\lambda}, 1_{r'\lambda'}) = &- \sum_{mn} \frac{b_{0m}^{r\lambda} b_{mn}^{r'\lambda'} \phi_n^{(0)}}{[h\nu_r + E_m^{(0)} - E_0^{(0)}][h(\nu_r + \nu_{r'}) + E_n^{(0)} - E_0^{(0)}]} \\ &- \sum_{mn} \frac{b_{0m}^{r'\lambda'} b_{mn}^{r\lambda} \phi_n^{(0)}}{[h\nu_{r'} + E_m^{(0)} - E_0^{(0)}][h(\nu_r + \nu_{r'}) + E_n^{(0)} - E_0^{(0)}]} \end{aligned} \tag{30}$$

$$\phi^{(0)}(2_{r\lambda}) = - 2^{1/2} \sum_{mn} \frac{b_{0m}^{r\lambda} b_{mn}^{r\lambda}}{[h\nu_r + E_m^{(0)} - E_0^{(0)}][2h\nu_r + E_r^{(0)} - E_0^{(0)}]} \cdot \text{etc.}$$

Further $E(_0{}^1)$ and $\phi(_0{}^1)$ vanish, and

$$E_0^{(2)} = - \sum_{r\lambda} \sum_m \frac{\left| b_{0n}^{r\lambda} \right|^2}{h\nu_r + E_m^{(0)} - E_0^{(0)}}$$

$$\phi_0^{(2)} = \sum_{r\lambda} \sum_m \sum_{n=0} \frac{b_{0m}^{r\lambda} \bar{b}_{mn}^{r\lambda} \phi_n^{(0)}}{[h\nu_r + E_m^{(0)} - E_0^{(0)}][E_n^{(0)} - E_0^{(0)}]} .$$

Moreover $\phi^1(_r1_\lambda)$, $\phi(_0{}^3)$ and $E(_0{}^3)$ vanish, and

$$\phi^{(2)}(1_{r\lambda}) = i \sum_{r'\lambda'} \sum_{mk} \sum_{n \neq 0} \frac{b_{0m}^{r'\lambda'} \bar{b}_{mn}^{r'\lambda'} b_{nk}^{r\lambda} \phi_k^{(0)}}{[h\nu_{r'} + E_m^{(0)} - E_0^{(0)}][h\nu_r + E_k^{(0)} - E_n^{(0)}][E_n^{(0)} - E_0^{(0)}]} \tag{32}$$

$$E_0^{(4)} = - \sum_{r\lambda} \sum_{r'\lambda'} \sum_{mk} \sum_{n \neq 0} \frac{b_{0m}^{r'\lambda'} \bar{b}_{mn}^{r'\lambda'} b_{nk}^{r\lambda} \bar{b}_{k0}^{r\lambda}}{[h\nu_{r'} + E_m^{(0)} - E_0^{(0)}][h\nu_r + E_k^{(0)} - E_n^{(0)}][E_n^{(0)} - E_0^{(0)}]}$$

etc.

The terms

$$-E_0^{(3)}\phi^{(0)}(1_{r\lambda})$$

and

$$-i\sum_P \sum_{\lambda' r'}\mu_P{}^{r'\lambda'}\phi^{(0)}(1_{r\lambda}1_{r'\lambda'}) - 2^{1/2}i\sum_P \mu_P{}^{r\lambda}\phi^{(0)}(2_{r\lambda})$$

in the equation for $\phi^{(3)}(1_{r\lambda})$ cancel, so that

$$\phi^{(3)}(1_{r\lambda})=0$$

and

$$\phi_0{}^{(5)}=0, \quad E_0{}^{(5)}=0.$$

The expansion for $E^{(0)}$ and $\phi^{(0)}$ can be continued, and only terms of even order in v/c appear.

It will be observed that the interaction terms in (31)

$$-\sum_{r\lambda}\sum_m [h\nu_r + E_m{}^{(0)} - E_0{}^{(0)}]^{-1}\left|\int \bar{\phi}_n{}^{(0)}\mu_P{}^{r\lambda}\phi_0{}^{(0)}d\boldsymbol{q}\right|\left|\int \phi_n{}^{(0)}\mu_{P'}{}^{r\lambda}\phi_0{}^{(0)}d\boldsymbol{q}\right| \tag{33}$$

$$\left[\text{we write } \int d\boldsymbol{q} \text{ for } \int\cdots\int dq_1{}^{(1)}\cdots dq_N{}^{(3)}\sum_{\sigma'\cdots\sigma N}\right]$$

differ from those computed for the second order from (28):

$$-\sum_{r\lambda}\sum_m (h\nu_r)^{-1}\left|\int \bar{\phi}_n{}^{(0)}\mu_P{}^{r\lambda}\phi_0{}^{(0)}d\boldsymbol{q}\right|\left|\int \bar{\phi}_n{}^{(3)}\mu_{P'}{}^{r\lambda}\phi_0{}^{(0)}d\boldsymbol{q}\right| \tag{34}$$

It is possible to express

$$\sum_{r\lambda}\frac{\mu_P{}^{r\lambda}\mu_{P'}{}^{r\lambda}}{h\nu_r + E_m{}^{(0)} - E_0{}^{(0)}}$$

in terms of the confluent hypergeometric functions, but the expressions are too complicated to be suitable for calculation.

The proper energy terms

$$-\sum_{r\lambda}\sum_P\sum_m \frac{\left|\int \bar{\phi}_m{}^{(0)}\mu_P{}^{r\lambda}\phi_0{}^{(0)}d\boldsymbol{q}\right|^2}{h\nu_r + E_m{}^{(0)} - E_0{}^{(0)}} = -\sum_{r\lambda Pm} T^{r\lambda}_{0m,P}$$

do not exist, although both

$$\sum_{r\lambda} T^{r\lambda}_{0m,P}$$

and

$$\sum_m T^{r\lambda}_{0m,P}$$

converge; for large ν_r,

$$\sum_m T^{r\lambda}_{0m,P} = 0(1)$$

and for large E

$$\sum_{r\lambda} T^{r\lambda}_{0m,P} = 0(1).$$

The energy level of the normal state is thus infinitely displaced by the interaction of the particles with the field; the question which we have now to consider is whether or not the energy differences between two states are displaced by a finite or an infinite amount.

In order to answer this question we must treat the case of energies which do not correspond to a normal state for the matter; and we have to modify (19), and take account of the emission of radiation by the system. And for this purpose it is convenient to make the dimensions L of the Hohlraum infinite, because that makes the physical interpretation of the solution more immediate. For then ν_r becomes continuous and we may normalize the $v_l{}^{r\lambda}(q_p)$ to the intervals $\Delta\nu\Delta\omega$, where $\Delta\omega$ is the element of solid angle of the unit vector ϵ_r. Furthermore we may treat here, to simplify the writing, the case that E corresponds to the first excited state of the atom, so that there is only one energy E_0 lower than E for which (20) is soluble.

We define the energy of the normal state by

$$E_0 = E_0{}^{(0)} + E_0{}^{(2)} + E_0{}^{(4)} \cdots \tag{35}$$

where $E_0{}^{(2)}$ and $E_0{}^{(4)}$ are given by (31) and (32), and we define the corresponding wave function

$$u_0 = \phi_0{}^{(0)} + \phi_0{}^{(2)} + \phi_0{}^{(4)} \cdots \tag{36}$$

where $\phi_0{}^{(2)}$ is given by (31). We can then extend this definition formally to obtain the energy and wave function of excited states:

$$\begin{aligned} E_m &= E_m{}^{(0)} + E_m{}^{(2)} + E_m{}^{(4)} \cdots ; \\ E_m{}^{(2)} &= -\int d\nu_r \int d\omega_r \sum_{\lambda} \sum_{n} \frac{|\, b^{r\lambda}_{mn} \,|^2}{h\nu_r + E_n{}^{(0)} - E_m{}^{(0)}} \\ u_m &= \phi_m{}^{(0)} + \phi_m{}^{(2)} + \phi_m{}^{(4)} \cdots \text{ etc.} \end{aligned} \tag{37}$$

But in the expressions for $E_m{}^{(2)}$ etc, and $\phi_m{}^{(2)}$ etc, the integrals over ν are now improper, and we have to displace the path of integration around the singularities. This is equivalent to replacing

$$\frac{1}{h\nu + E_n{}^{(0)} - E_m{}^{(0)}} \quad \text{for} \quad E_n{}^{(0)} < E_m{}^{(0)}$$

by

$$\frac{1}{h\nu + E_n{}^{(0)} - E_m{}^{(0)}} \pm i\pi\delta(h\nu + E_n{}^{(0)} - E_m{}^{(0)}) \tag{38}$$

and then taking the principal value of the integrals over ν. Then in general all the E_m's except E_0 are complex. We now transform the $\phi(M_{r\lambda}, q_p\sigma_p)$ by the formulae

$$\phi(M_{r\lambda}, m) = \sum_{\sigma P} \int \cdots \int dq_1^{(1)} \cdots dq_N^{(3)} u_m(q_P, \sigma_P) \tag{39}$$

$$\phi(M_{r\lambda}, q_P, \sigma_P)$$

and introduce

$$\overset{r\lambda}{\mu}_{mn,P} = \sum_{\sigma P} \int \cdots \int dq_1^{(1)} \cdots dq_N^{(3)} \bar{u}_m \mu_P \overset{r\lambda}{} u_n . \tag{40}$$

Then if the $\phi(M, m)$ satisfy the equations, which follow from (11):

$$\begin{aligned}(-E+E_m)\phi(0,m) = &-i\int d\nu_r \int d\omega_r \sum_{\lambda} \sum_{P} \overset{r\lambda}{\mu}_{0m,P} F_1(\omega_r \lambda)\delta\left(\nu_r + \frac{E_0 - E}{n}\right) \\ &- \int d\nu_r \int d\omega_r \sum_{\lambda} \sum_{P} \overset{r\lambda}{\mu}_{nm,P} \int d\nu_r' \int d\omega_r' \sum_{\lambda'} \sum_{P'} \overset{r'\lambda'}{\mu}_{0n,P'} F_2(\omega_r, \omega_r', \nu_r', \lambda, \lambda') \\ &\delta\left(\nu_r + \nu_r' + \frac{E_0 - E}{h}\right) + \cdots \end{aligned} \tag{41}$$

$$\begin{aligned}\phi(1_{r\lambda}, 1m) = &\, i \sum_{Pn} \overset{r\lambda}{\mu}_{nm,P} \phi(0,n) \left\{ \frac{1}{-E + h\nu_r + E_m} + \frac{i\pi\delta_{m0}}{h}\delta\left(\nu_r + \frac{E_m - E}{h}\right)\right\} \\ &+ F_1(\omega_{r\lambda})\delta\left(\nu_r + \frac{E_m - E}{h}\right) - i \sum_{P} \int d\nu_r' \int d\omega_r' \sum_{\lambda'} \overset{r\lambda}{\mu}_{0m,P} \\ &F_2(\omega_r', \omega_r, \nu_r', \lambda, \lambda')\delta\left(\nu_r + \nu_r' + \frac{E_0 - E}{h}\right) \cdots \end{aligned} \tag{42}$$

$$\begin{aligned}\phi(1_{r\lambda}, 1_{r'\lambda'}, m) = &\, i \sum_{Pm} \left\{ \overset{r'\lambda'}{\mu}_{nm,P} \phi(1_{r\lambda}, n) + \overset{r\lambda}{\mu}_{nm,P} \phi(1_{r'\lambda'}, n)\right\} \\ &\left\{ \frac{1}{-E + h(\nu_r + \nu_{r'}) + E_m} \pm \frac{i\pi\delta_{m0}}{h}\delta\left(\nu_r + \nu_{r'} + \frac{E_m - E}{h}\right)\right\} \\ &+ F_2(\omega_r, \omega_r', \nu_r', \lambda, \lambda')\delta\left(\nu_r + \nu_r' + \frac{E_0 - E}{h}\right) \cdots \end{aligned}$$

where now the functions F are completely arbitrary, then the $\phi(M_{r\lambda}, q_p, \sigma_p)$ satisfy (11); for each choice of these F's we can obtain a solution of (11). Now the terms

$$\frac{\overset{r\lambda}{\mu}_{nm,P}\phi(0,n)}{-E + h\nu_r + E_m} \text{ etc.}$$

give a radiation field which does not extend to infinity; and the terms

$$\frac{\pm i\pi \overset{r\lambda}{\mu}_{nm,P}}{h}\phi(0,n)\delta_{m0}\delta\left(\nu_r + \frac{E_0 - E}{h}\right) \text{ etc.}$$

represent outgoing[8] electromagnetic waves, so that by the choice of the F's

[8] P. A. M. Dirac, Zeits. f. Physik **44**, 585 (1927).

we may determine the radiation incident upon the system. The simplest case is that in which only quanta of the single frequency

$$\nu=\frac{1}{h}(E-E_0)=\nu_r \tag{43}$$

are incident upon the system, so that all the F's vanish except

$$F_1(\omega,\lambda).$$

For this case

$$\phi(0,m)=+\frac{i\sum_{\lambda}\sum_{P}\int d\omega_r \mu_{0m}^{r\lambda}{}_{,P}F_1(\omega,\lambda)}{E-E_m}=\frac{iG_m{}^{\nu}}{E-E_m}. \tag{44}$$

Now by hypothesis E is to be chosen that only one E_m-E, that for $m=1$, say, is to be small, so that only

$$\phi(0,1)=\frac{iG_1{}^{\nu}}{E-E_1} \tag{45}$$

is large. The probability of absorption to this state is thus proportional to

$$\frac{|G_1{}^{\nu}|^2}{|E-E_1|^2}=\frac{|G_1{}^{\nu}|^2}{|h\nu+E_0-E_1|^2} \tag{46}$$

so that the shape of the absorption line is given by

$$\frac{\text{const.}}{\left|\nu+\frac{1}{h}(E_0-E_1)\right|^2} \tag{47}$$

since $G^{\nu}{}_r$, varies slowly with ν.

If we evaluate E_0, E_1 to the second order in v/c, and drop the higher terms—and this is equivalent to neglecting transitions in which more than one quantum plays a part—(47) reduces to

$$\frac{\text{const.}}{\left[\nu+\frac{1}{h}(E_0{}^{(0)}-E_1{}^{0})+\frac{1}{h}(E_0{}^{(2)}-\frac{1}{2}E_1{}^{(2)}-\frac{1}{2}\overline{E}_1{}^{(2)})\right]+\frac{1}{4h^2}|E_1{}^{(2)}-\overline{E}_1{}^{(2)}|^2}. \tag{48}$$

The absorption line is thus of the same shape as that predicted on the basis of the correspondence principle, and that found, for this case, by Dirac[8], and the half-breadth of the line is

$$\left|\frac{E_1{}^{(2)}-\overline{E}_1{}^{(2)}}{2h}\right|=\frac{\pi}{h}\int d\omega\sum_{\lambda}|b_{01}^{r\lambda}|^2=\frac{1}{4\pi\tau_1} \tag{49}$$

where τ_1 is the natural life time of the state 1.

The center of the absorption line is displaced to the red from $(1/h)$ $(E_1^{(0)} - E_0^{(0)})$ by an amount

$$\frac{1}{h}\left(E_0^{(2)} - \frac{1}{2}E_1^{(2)} - \frac{1}{2}\overline{E}_1^{(2)}\right)$$

$$= \frac{1}{h}\int d\nu \int d\omega \sum_{\lambda} \sum_{n} \left\{ \frac{\left| b_{1n}^{r\lambda} \right|^2}{h\nu + E_n^{(0)} - E_1^{(0)}} - \frac{\left| b_{0n}^{r\lambda} \right|^2}{h\nu + E_n^{(0)} - E_0^{(0)}} \right\}$$

$$\sim \frac{1}{h}\int d\nu \int d\omega \sum_{\lambda} \sum_{n} \sum_{pp'} \left\{ \frac{\mu_{1n,p}^{r\lambda} \cdot \mu_{n1,p'}^{r\lambda}}{h\nu + E_n^{(0)} - E_1^{(0)}} - \frac{\mu_{0n,p}^{r\lambda} \cdot \mu_{n0,p'}^{r\lambda}}{h\nu + E_n^{(0)} - E_0^{(0)}} \right\}. \quad (50)$$

Here the principle values are to be taken for all improper integrals over ν. The terms for $p \neq p'$ are just those to be expected from (33) for the displacement of the energy levels by the magnetic interaction of the particles. The terms

$$\frac{1}{h}\int d\nu \int d\omega \sum_{\lambda} \sum_{n} \left\{ \frac{\left| \mu_{1n,p}^{r\lambda} \right|^2}{h\nu + E_n^{(0)} - E_1^{(0)}} - \frac{\left| \mu_{0n,p}^{r\lambda} \right|^2}{h\nu + E_n^{(0)} - E_0^{(0)}} \right\} \quad (51)$$

must be ascribed to the effect of the interaction of the particle with its own field. They may be compared with the formula obtained[8] for the same effect by Dirac, who finds a displacement

$$\frac{1}{h}\int d\nu \int d\omega \sum_{\lambda} \frac{\left| \mu_{01,p}^{r\lambda} \right|^2}{h\nu + E_0^{(0)} - E_1^{(0)}}. \quad (52)$$

There does not appear to be any justification for this result, because in its derivation terms were neglected that are of the same order as those retained. But it is of interest to observe that the integral in (52) exists, and gives a finite displacement of the line of the second order in v/c. This displacement is thus larger than the natural line breadth, which is of the third order. It can be computed[9] when the u's are known. Thus for the first Lyman doublet of hydrogen we find the same displacement, in this order, for both components; it turns out to be

$$+\frac{ch}{32\pi^2 e^2}\frac{1}{\tau_1} = \frac{ch}{32\pi^2 e^2} A_{10}$$

which is about forty times the line breadth. The fact that this term, and the similar terms in (51), are the same, in second order, for the two components of the doublet, suggests that the formulae (33) in which the proper energy is neglected, will give the atomic fine structure splitting correct to the second order.

If we try to compute the displacement from (51), we find that the integrals over ν diverge logarithmically for high frequencies. One can readily

[9] The calculations of the displacements predicted by the results of Dirac were carried through in collaboration with Harvey Hall; and I am indebted to him for permission to quote them here. One must use the retarded potentials to obtain a convergent integral.

see that this is not the result of the neglect of higher order terms, nor of any of the approximations made in the work. The theory thus leads to the false prediction that spectral lines will be infinitely displaced from the values computed by the Bohr frequency condition. The behavior of the expression (51) calls for some comment. As the formula stands, the integral over ν diverges absolutely; this may be verified by evaluating the terms for a free particle. But the question arises whether it is possible so to rearrange the order of the integration over ν the summation over n, and the two integrations involved in the evaluation of the μ_{mn}'s by (40), that the limit $n\to\infty$, $\nu\to\infty$ exists. This cannot be effected by an interchange of the sum over n and the integral over ν; but there is a procedure which, when the E's in the resonance denominators of (51) are dropped, does give an absolutely convergent result. This procedure was suggested by Heisenberg, who showed that, if we first perform the integration over ν and ω and the summation over λ, then sum over all the states n of the same energy, then sum these up to some large but finite energy E, take the difference of the two terms for the state (0) and the state (1), then perform the two integrations over the configuration space, and finally allow E to become infinite, the limit $E\to\infty$ exists, and (51) tends to zero. But if we try to apply this procedure to (51) when the E terms are not dropped, we get for the leading term the divergent result

$$4e_p^2/hc\cdot(E_1^{(0)}-E_0^{(0)})/h\cdot\int^\infty dx/x \tag{53}$$

Nor is there any method for obtaining an absolutely convergent expression for (51). It should be observed that (53) gives us another justification for using (33) to get the fine structure separations correct to the second order.

One can see quite simply that (47) ought not to give a finite line displacement. For consider two states of a free particle; in one let the particle be at rest; in the other let it have the velocity v. Then if the energy of the particle at rest be E, the energy of the moving particle in proper coordinates moving with the particle will also be E. But we know how this energy transforms under a Lorentz transformation; in the original coordinates it will be

$$E\beta \qquad \beta=[1-(v/c)^2]^{-1/2}$$

and in the same coordinates the difference in energy of the two states, which gives the line displacement, will be

$$E(\beta-1)$$

But this can only be finite if E is finite which, by (31), it is not.

We have treated these difficulties in some detail, because they show that the present theory will not be applicable to any problem where relativistic effects are important, where, that is, we cannot be guided throughout by the limiting case $c\to\infty$. The theory can thus not be applied to a discussion of the structure of the nuclei. It appears improbable that the difficulties discussed in this work will be soluble without an adequate theory of the masses of electron and proton; nor is it certain that such a theory will be possible on the basis of the special theory of relativity.

THE EFFECT OF END LOSSES ON THE CHARACTERISTICS OF FILAMENTS OF TUNGSTEN AND OTHER MATERIALS

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(Received September 20, 1929)

Abstract

The leads of a tungsten filament in vacuum cool the ends of the filament and so affect the voltage, candle power, electron emission and other properties of the filament. For long filaments, where there is a central portion at a uniform temperature T_m, the temperature distribution near the lead is derived. A method for determining T_0, the temperature of the lead-filament junction, is given. Tables and formulas are presented which allow ready calculation of the effect of the leads on the properties of any long tungsten filament for which the current and diameter are known. From the more general results it has been found that the decrease in voltage due to the cooling of one lead may be represented by $\Delta V = 0.154\ (T_m/1000) - 0.081\ (T_o/1000) - 2.1 \cdot 10^{-8}\ T_o T_m - 0.056$. There is an extension of the theory to cover the cases of filaments in gases, filaments of other materials, etc.

Part II of the paper gives figures from which may be found the properties of filaments so short that the first theory does not apply. Some experimental checks of the theory are given.

In general the results and the methods of application have been placed first, and the mathematical derivations have been placed at the end of each part.

For a short filament with leads cooled in liquid air a negative slope of the volt-ampere characteristic when the central temperature is much smaller than T_m is observed.

Part I. The Long Filament

THE extensive use of tungsten filaments in research and industry makes it important to consider how the cooling effects of the leads influence the characteristics of such filaments. For wide ranges of temperature the characteristics of hypothetical filaments which are not cooled by leads may be found from tables of the properties of tungsten[1-7] The magnitudes of the lead losses have been evaluated experimentally[1, 8, 9] and by theoretical methods.[10] It is felt that there is still a place for a systematic treatment

[1] W. E. Forsythe and A. G. Worthing, Astrophys J. **61,** 146 (1925).
[2] C. Zwikker, Royal Acad. Amsterdam **34,** No. 5 (1925).
[3] H. A. Jones and I. Langmuir, G. E. Review **30,** 310, 354, 408 (1927).
[4] H. A. Jones, Phys. Rev. **28,** 202 (1926).
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[8] A. G. Worthing, Journ. Frank. Inst. **194,** 597 (1922).
[9] T. H. Amrine, Trans. Ill. Eng. Soc. **8,** 385 (1913).
[10] A. G. Worthing, Phys. Rev. **4,** 524 (1914); R. Ribaud and S. Nikitine, Ann. de Physique **7,** 5 (1927); V. Bush and K. E. Gould, Phys. Rev. **29,** 337 (1927).

which may be conveniently applied to a filament operated under any ordinary conditions.[11]

Temperature distribution. For most tungsten filaments the cooling effect of the leads does not extend appreciably to the central portion of the filament. The absolute temperature, T_m, of this portion may be calculated from the diameter of the filament and the current through it.[12] The temperature of other parts of the filament is best expressed as a fraction, θ, of T_m. Thus $\theta = T/T_m$, where T represents the absolute temperature of any point of the filament.

We may consider the effect of each lead independently, since the two effects do not overlap. Of fundamental importance is the variation of θ with x, the distance from the lead. This is shown later to be governed by the equation,

$$\phi = a d\theta/dx \tag{1}$$

where ϕ is a function of θ, and is given by Eq. (30). a is a parameter of the dimension of length, and depends on T_m and the filament diameter D.

TABLE I. *Values of a_0 for various values of T_m. (For 'a' use Eq. (2).)*

T_m(°K)	a_0(cm)	T_m	a_0	T_m	a_0
600	5.84	1700	0.646	2800	0.275
700	4.08	1800	.582	2900	.261
800	3.01	1900	.527	3000	.247
900	2.33	2000	.481	3100	.235
1000	1.863	2100	.441	3200	.223
1100	1.524	2200	.406	3300	.213
1200	1.274	2300	.377	3400	.209
1300	1.084	2400	.351	3500	.195
1400	.936	2500	.329	3600	.187
1500	.821	2600	.309	3655	.183
1600	.724	2700	.291		

a_0, the value of a for $D = 0.01$ cm (4 mil approx.) is given in Table I. a for other values of D may be found from

$$a = a_0(D/0.01)^{1/2}. \tag{2}$$

Integration of (1) gives

$$(x/a)_0^\theta = \int_0^\theta d\theta/\phi. \tag{3}$$

The values of $(x/a)_0^\theta$ for various values of θ are tabulated in the second column of Table II. Note that a is effectively a unit of length. The symbol $(x/a)_{\theta_1}^{\theta_2}$ will in general represent the distance, expressed in a-units, from a point at temperature $\theta_1 T_m$, to a point at temperature $\theta_2 T_m$. To obtain dis-

[11] I. Langmuir, Trans. Faraday Soc. **17**, 634 (1922). See also references (7) p. 210, (6) p. 312, (3) p. 356. In these papers formulas for ΔV and ΔV_H are given. They were derived by methods similar to the ones used in this paper.

[12] Ref. (3), p. 312, Table I, column 4.

tance in a-units, divide the distance x in cm by the value of a, in cm, found from Table I.

TABLE II. *Values of* $(x/a)_0^\theta$ *and* $\beta(\theta_0)$.
For $n>4$: $\beta(\theta_0)=(x/a)_0^{\theta_0}$. For $n=1.2$, see columns 3 and 6.

θ	$(x/a)_0^\theta$	$\beta(\theta_0)$ $n=1.2$	θ	$(x/a)_0^\theta$	$\beta(\theta_0)$ $n=1.2$
0.0	0.000	0.000	0.7	0.7394	0.464
.1	.0419	.040	.8	.9766	.532
.2	.1110	.102	.85	1.1354	
.25	.1522	.137	.9	1.3592	.598
.3	.1974	.172	.95	1.7260	.630
.4	.2999	.245	.99	2.5535	.654
.5	.4200	.320	.999	3.7224	.659
.6	.5628	.392	1.000		.660

The temperature distribution near a cooling lead is represented by the curve farthest to the right (labeled 0.995) in Fig. 2 (Part II). The increment in the abscissa $(x/a)_{\theta}^{\theta_2}$ from the ordinate θ_2 to ordinate θ_1 gives the distance along the filament from a point at temperature $\theta_1 T_m$ to a point at temperature $\theta_2 T_m$.

In practice the junction of lead and filament will be at a temperature $T_0=\theta_0 T_m$. The exact determination of this temperature is rather difficult. If the leads are short and fairly heavy we may assume $T_0=T_R$, where T_R is the room temperature. The error due to this assumption in the value of any filament-property for the whole filament[13] computed by the methods of this paper will be less than 1 percent when the length of the lead is less than a certain maximum length l_0. We find that l_0 is given approximately by

$$l_0 = 0.32(x/a)(D_L/0.1)^2(\lambda_L/0.586)/A. \qquad (4a)$$

A is the filament current in amperes and (x/a) represents the half length of the filament. D_L is the lead diameter in cm. λ_L is the thermal conductivity of the lead in watts cm^{-1} deg^{-1}. For nickel leads $\lambda_L/0.586=1$, for tungsten leads $\lambda_L/0.586=2.73$, for molybdenum $\lambda_L/0.586=2.49$.

Thus with nickel leads for which $D_L=0.1$ cm and $l<1.6$ cm, used with a 20 cm filament of $D=0.02$ cm for which the highest operating temperature is $T_m=2400°$ we may assume $T_0=T_R$, since we find $A=4.02$,[12] $x/a=20.2$, and thence from Eq. (4a) $l_0=1.6$ cm.

For leads such as those used in incandescent lamps it is sufficiently accurate for many purposes to assume that $T_0=(1/4)T_m$.

If desired we may evaluate $\Delta T=T_0-T_R$ in terms of the lead length l. We find that

$$\Delta T = l \cdot A\,(0.586/\lambda_L)(0.1/D_L)^2\,(\Delta T_0). \qquad (4b)$$

$(\Delta T)_0$ is the value of ΔT for a nickel lead for which $D_L=0.1$ cm, $l=1$ cm and $A=1$ amp. It is given in Table III as a function of the value of T_m for the filament. Note that these values are for a filament of constant current,

[13] Such as the voltage or the candle power of the whole filament.

and hence that the diameter of a filament for which $\Delta T=(\Delta T)_0$ is smaller for the higher temperatures in the table.

The data from Table III are not dependable above $T_0=1000°$, where radiation loss is appreciable, nor when the resistance loss in the lead is large.

TABLE III. $(\Delta T)_0=T_0-T_R$ *for nickel leads when* $A=1$, $D_L=0.1$, $l=1$.

T_m(°K)	$(\Delta T)_0$	T_m	$(\Delta T)_0$	T_m	$(\Delta T)_0$
1000°	21°	1800°	45°	2800°	80°
1200	26	2000	51	3000	87
1400	32	2200	58	3200	95
1600	38	2400	65	3400	102
		2600	72		

The actual temperature distribution of the filament is given by (cf. Eq. (3))

$$(x/a)_{\theta_0}^{\theta}=\int_0^{\theta}d\theta/\phi-\int_0^{\theta_0}d\theta/\phi. \tag{5}$$

To find the distance from the lead, x, of a point of known temperature θ, we may evaluate the two integrals above by means of Table II, and then obtain x from $(x/a)_{\theta_0}^{\theta}$ by using Table I. Conversely we may find the temperature θ of a point at any given distance, x.

By the use of data on the characteristics of tungsten filaments as functions of temperature,[1, 3] and from the temperature distribution along a filament as found above, the properties of the filament at each point can be calculated. For example, we can determine the electron emission, the radiated energy, the luminous intensity, et cetera, at each point.

The effect of lead losses on filament characteristics. Many filament properties which are functions of the temperature would be strictly proportional to the length of the filament if the temperature were everywhere uniform. Let h be a quantity which measures some one of these properties *per unit length* at any given absolute temperature T. For example, h may represent the voltage drop per cm or the electron emission per cm of length. Let h_m be the value of h at the temperature T_m. Nearly all the properties of tungsten which we shall need to consider vary in proportion to some definite power of the temperature over rather wide ranges. Thus we may put

$$h=h_m\theta^n \tag{6}$$

$$n=(dh/h)(T/dT) \tag{7}$$

where n is approximately constant.[14]

If a filament of length $2x$ were all at its maximum temperature T_m the value H_m of any property for the whole filament would be

$$H_m=2xh_m. \tag{8}$$

[14] For values see Ref. 3, p. 354 Table II or Ref. 1, p. 153 Table I-*B*.

The cooling effect of the leads makes H, the actual value of the property for the whole filament, less than H_m. ΔH, the amount of this decrease due to one lead, may be thought of as the total value of the property over a short length of uncooled filament. Designate by ΔV_H the voltage drop across this length. ΔV_H is then the volt-equivalent of ΔH, and the fractional decrease of H_m can thus be expressed as a fraction of the total voltage V_m

$$\Delta V_H/V_m = \Delta H/H_m. \tag{9}$$

The ratio H/H_m is a measure of the extent to which the cooling effect changes the property. We have

$$H/H_m = (H_m - 2\Delta H)/H_m = (V_m - 2\Delta V_H)/V_m. \tag{10}$$

The factor 2 accounts for two leads.

TABLE IV. *Values of* $B_1 = \int_0^1 (1-\theta^n)d\theta/\phi$.

n	B_1	n	B_1	n	B_1
1	0.583	9.0	1.626	20	2.032
1.2	0.660	10	1.682	22	2.079
2.0	0.882	11	1.728	24	2.124
3.0	1.076	12	1.772	25	2.145
4.0	1.217	13	1.813	26	2.165
5.0	1.329	14	1.850	28	2.203
5.1	1.339	15	1.885	30	2.238
6.0	1.421	16	1.918	35	2.315
7.0	1.500	17	1.949	40	2.384
8.0	1.566	18	1.978	50	2.497
		19	2.006	60	2.589

If V is the actual voltage drop (in volts) and ΔV the value which ΔH has when the property measured by H is voltage

$$H/H_m = (V+2\Delta V - 2\Delta V_H)/(V+2\Delta V). \tag{11}$$

It will be shown later that the value of ΔV_H is given by

$$\Delta V_H = 1.812 \cdot 10^{-5} T_m^{1.3}[B_1 - \beta(\theta_0)]. \tag{12}$$

B_1 is given in Table IV. It is a function of n, the temperature exponent for the property H in question. For $n>5$, B_1 is given by the equation

$$B_1 = 0.5170 + 1.1660 \log_{10} n - 0.0591/n + 0.2224/n^2 + 0.0140/n^3 - 0.468/n^4 + \cdots. \tag{13}$$

The coefficient of Eq. (12), $1.812 \cdot 10^{-5} T_m^{1.3}$, is given in Table V.

$\beta(\theta_0)$ in Eq. (12) is a function of θ_0. It is independent of n if $n>4$ and $\theta_0<0.5$, and is given by

$$n>4, \theta_0<0.5 \quad \beta(\theta_0) = (x/a)_{0^\circ}^{\theta^\circ}. \tag{14}$$

This value of x/a is to be taken directly from Table II for $\theta=\theta_0$. For $n=1.2$ (the exponent for resistance and the only important small value of n) $\beta(\theta_0)$ is given in the third column of Table II.

TABLE V. $1.812 \cdot 10^{-5} T_m^{1.3}$

T_m	$1.812 \cdot 10^{-5} T_m^{1.3}$	T_m	$1.812 \cdot 10^{-5} T_m^{1.3}$
1000°	0.1439	2300°	0.4250
1100	.1629	2400	.4493
1200	.1825	2500	.4737
1300	.2024	2600	.4985
1400	.2229	2700	.5236
1500	.2438	2800	.5490
1600	.2651	2900	.5744
1700	.2869	3000	.6003
1800	.3091	3100	.6266
1900	.3316	3200	.6528
2000	.3544	3300	.6797
2100	.3777	3400	.7066
2200	.4011	3500	.7337

Since the current is constant, the voltage has the same temperature exponent as the resistance. Hence ΔV may be found from Eq. (12) by setting $n = 1.2$. In many cases to apply Eq. (11) it may be easier to find the theoretical voltage $V_m = V + 2\Delta V$ directly from the resistivity at T_m and the filament dimensions. The wattage *input* depends on the resistance of the filament and hence ΔV_H in this case is to be found for $n = 1.2$. The wattage *radiated* on the other hand depends on $n = 5.1$ or thereabouts.[15]

Method of application. In finding the value of B_1 for Eq. (12) from the value of n, we notice that for most properties of tungsten n is not constant as was assumed, but varies slightly with the temperature. We must take a mean value of n, that is, its value at some effective temperature T_E. This temperature is roughly that at which $h = h_m/2$. This temperature and the corresponding value of n may be found directly.[14]

As an alternate method to find T_E we note that for some properties h may be quite accurately expressed as

$$h = CT^k e^{-b/T}. \tag{15}$$

Thus for candle power Wiens' law (using a Crova wave-length) gives $k = 0$, $b = 25200°$. The Richardson-Dushman equation for the electron emission from pure tungsten has $k = 2$, $b = 52600°$. The rate of evaporation of a tungsten filament is expressed by Eq. (15) with $k = 0$, $b = 94100°$. Setting $h = h_m/2$ in Eq. (15) and using Eq. (6) to evaluate the term in k, we find approximately

$$b/T_E = b/T_m + [1 - k/n] \log_e 2. \tag{16}$$

Differentiating Eq. (15) and comparing with Eq. (7) we see that

$$n = k + b/T. \tag{17}$$

Hence from Eq. (16) and the values of the constants given above we obtain the following equations for effective values of n in terms of T_m

$$\text{candle power } n = 25200°/T_m + 0.7 \tag{18}$$

[15] Ref. 3, p. 312, Table I, column 5.

$$\text{electron emission } n = 52600°/T_m + 2.6 \tag{19}$$

$$\text{evaporation } n = 94100°/T_m + 0.7. \tag{20}$$

The decrease in the rate of evaporation near the leads is ordinarily not a matter of experimental interest, but under certain conditions its effects may be directly observed. Nitrogen or carbon monoxide in the presence of a tungsten filament at very high temperatures gradually disappears because every atom of tungsten which evaporates combines with a molecule of the gas to form a stable and non-volatile compound. Thus the rate of "clean-up" of the gas depends on the total amount of metal that evaporates.

The direct application of Eq. (12) as outlined above is the most accurate method for the evaluation of ΔV_H. In many cases where only approximate results are desired ΔV_H may be found from the following empirical equations, which were found to fit the data calculated from Eq. (12). The deviation from the results of Eq. (12) is less than the amount tabulated for the given range. The actual error of the results may in some cases be larger than this, due to approximations in the derivation of Eq. (12).

TABLE VI. $\Delta V_H = P(T_m/1000) - Q(T_0/1000) - R$ *volts.*

H is	P	Q	R	Range—T_m	Range—T_0	Range—ϑ_0	Max. error (volts)
Voltage*	0.154*	0.081*	0.056*	1000–2500°	any values	0.1–0.5	0.004
Candle Power	.338	.182	− .004	600–3500	300–1400°	.1– .5	.01
Electron emission	.440	.158	.072	1000–3500	300– 900	.07–.5	.009
Evaporation	.480	.160	.060	1500–3500	300– 900	.07–.5	.008
Watts radiated	.293	.160	.084	1100–3000	300– 900	.1– .4	.01

* For voltage (Watts input) a term $-2.1 \cdot 10^{-8} T_0 T_m$ is to be added to the right hand side of Eq. (21).

In many cases with short, heavy leads $T_0 = 300°$. In these circumstances the following approximate equations hold.

TABLE VII. $\Delta V_H = P_0(T_m/1000) - S$ *volts* (22

H is	P_0	S	Range—T_m	Max. error (volts)
Voltage	0.148	0.080	1000–2500	0.004
Candle Power	.338	.051	600–3500	.01
Electron Emission	.439	.119	1000–3500	.007
Evaporation	.477	.103	1500–3500	.001
Watts radiated	.287	.121	1000–3100	.01

Computation of T_m. If we know the diameter of a filament and the current through it, T_m may be obtained directly from Tables which give temperature tabulated against current divided by $d^{3/2}$.[12]

If the diameter is not known, but if the length $2x$ is known, the voltage V and amperage A corresponding to the temperature we wish may be found. Assuming that the filament is all at the maximum temperature T_m, we compute $VA^{1/3}/(2x)$ and find a first approximation for T_m.[16] For

[16] Ref. 3, p. 312, Table I, column 6 gives $VA^{1/3}/(2x)$ as a function of T.

this value of T_m there is a certain voltage correction ΔV. This gives us a much better value, $V+2\Delta V$, for the voltage if the filament were all at T_m. $(V+2\Delta V)\,A^{1/3}/(2x)$ then gives us a second approximation for T_m. As many approximations as desired may be made.

Shorter filaments. With shorter filaments the cooling effects of the two leads overlap, and the temperature at any point may be found approximately by adding the cooling effect of each lead at that point. With still shorter filaments these temperatures and the values of H/H_m found as above are in error. The amount of the error depends on n, the temperature exponent of the property in question. Part II, Table X gives in column 2 the maximum value of the half length $(x/a)_0^{\theta_c}$ for which the error in H/H_m is less than 1 percent. Column 3 gives similar information for 5 percent error. For details see Part II.

Derivation of the Equations

The fundamental differential equation giving the temperature distribution near a cooling lead is[8]

$$A^2r+[\lambda(d^2T/dx^2)+(d\lambda/dT)(dT/dx)^2]\pi D^2/4=w. \tag{23}$$

The symbolism is explained in Table VIII. The terms A^2r and w correspond respectively to the rate of production of energy and the rate of radiation

Table VIII. *Symbols.*

A	Filament current in amps	w	$=h$ for power radiated
D	Filament diameter (cm)	r	$=h$ for resistance
D_L	Lead diameter (cm)	v	$=h$ for voltage drop
l	Length of lead (cm)	H	Value of any property for the whole filament
x	Distance along filament (cm)		
a	Unit of length (cm) Table I	H_m	Value of H if the whole filament were at T_m
a_0	a for $D=0.01$ cm		
sub m	Value at the uncooled central portion of the filament	V	$=H$ for voltage drop
		H_c	Value of H if the whole filament were at T_c
sub c	Value at the center of the filament (Part II)	n	Temperature exponent for any property $=d\log h/d\log T$
T	Absolute temperature		
T_R	Room temperature	ρ	$=n$ for resistance
$T_0=\theta_0T_m$	Lead-filament junction temperature	ω	$=n$ for radiation
ΔT	$=T_0-T_R$	k	$=n$ for thermal conductivity
θ	$=T/T_m$	ϕ	$=ad\theta/dx$
$(x/a)_{\theta_1}^{\theta_2}$	Distance in a-units from point at θ_1 to point at θ_2	ΔV_H	see Eq. (12)
		B_1	Table IV
λ	Thermal conductivity of filament	$B_{1\delta}$	Value of B_1 for $\omega=5$
λ_L	Thermal conductivity of lead	$\beta(\theta_0)$	Table II
h	Value of any property per cm of filament length	τ_0	$=T_o/T_c$

of energy per unit length of filament, while the expression involving λ corresponds to the net rate of conduction of energy into an element of the filament.

An inspection of tables giving the characteristics of tungsten filaments as functions of the temperature shows that it is possible to express Eq. (23) in a much simpler form.[3]

The resistance of a tungsten filament can be expressed quite accurately over a wide range of temperatures by the equation $r=cT^{\rho}$, where c is a constant and $\rho=1.20$ (for the range between 600°–3,000°K). Similarly the radiated power may be expressed approximately by the relation $w=c'T^{\omega}$, where ω is fairly constant, having the values, 5.65 at 1,000°K, 5.12 at 1700°, 4.93 at 2,000°, 4.71 at 2,400° and 4.48 at 3,000°. In the majority of experiments in which it is desired to calculate the cooling effect of the leads the temperature of the hottest part of the filament will probably be below 2,400°. By averaging the values of this exponent from 2,000° to 400°, weighing each in proportion to the corresponding value of w, the effective exponent is found to be 5.1. We shall, therefore, take this to be the value of ω. Even at very high filament temperatures, where the effective exponent would be about 4.7, we shall see that the error made by using $\omega=5.1$ is practically negligible.

The heat conductivity of tungsten at temperatures from 1,300 to 2,500° has been given by Forsythe and Worthing.[1] It ranges from 0.93 watts cm^{-1} deg^{-1} at 1,300° to 1.21 at 2,500°. We find that the empirical equation

$$\lambda=0.840(T/1000)^{0.4} \tag{24}$$

expresses the values of λ at the 13 observed points given in their table (at 100° intervals) within an error of 0.0022 or about 0.2 percent. This equation is used throughout this paper.

In the central uncooled portion w_m, the power radiated per unit length, is equal to A^2r_m, where r_m is the resistance per unit length at this place. Since A is constant throughout the length of the filament, the temperature exponent of A^2r is the same as that of r, that is ρ. Hence we can replace the first term in Eq. (23) by $w_m\theta^{\rho}$. Similarly w may be replaced by $w_m\theta^{\omega}$. From Eq. (24) we obtain the relation $\lambda=\lambda_m\theta^{0.4}$, where λ_m is the thermal conductivity at temperature T_m. Using the values of λ and $d\lambda/dT$ from this relation, we obtain from Eq. (23)

$$d^2\theta/dx^2+0.4(d\theta/dx)^2/\theta=(\theta^{\omega-0.4}-\theta^{\rho-0.4})/a^2 \tag{25}$$

where a is a parameter defined by

$$a^2 = \pi D^2\lambda_m T_m/4w_m. \tag{26}$$

We can replace w_m by its value v_m^2/r_m where v_m is the voltage drop per cm at temperature T_m. The factor r_mD^2 which then occurs in the equation is independent of D and varies as $T_m^{1.2}$ (it is in fact the function R' given by Jones and Langmuir).[3] Thus

$$r_mD^2=7.89\cdot10^{-9}T_m^{1.2}. \tag{27}$$

From Eqs. (24), (26), (27)

$$a=1.812\cdot10^{-5}T_m^{1.3}/v_m. \tag{28}$$

In computing a from this equation v_m was found from Tables of characteristics.[13] Since $v_m \propto D^{-1/2}$, we obtain Eq. (2).

In Eq. (25) set $\omega = 5.1$, $\rho = 1.2$ and substitute ϕ as defined by Eq. (1) for x

$$\phi d\phi/d\theta + 0.4\phi^2/\theta = \theta^{4.7} - \theta^{0.8}. \tag{29}$$

By taking as new variables ϕ^2 and $\log \theta$ this equation becomes linear and may be solved in the usual way to give

$$\phi^2 = (3 - 5\theta^{2.6} + 2\theta^{6.5})/6.5\theta^{0.8}. \tag{30}$$

The constant of integration, 3, is fixed by the condition that $d\theta/dx = 0$, and therefore $\phi = 0$ at $\theta = 1$, the center of the filament.

For values of θ close to unity (30) may be expanded in terms of $Z = 1 - \theta$

$$\phi^2 = 3.9Z^2 - 4.81Z^3 + 3.715Z^4 - 0.8886Z^5 + 0.4068Z^6 + 0.27Z^7 + \cdots. \tag{31}$$

Temperature distribution. When $\theta \leqq 0.6$ the integral in Eq. (2) may be found by expanding $1/\phi$ in the series

$$1/\phi = 1.472\theta^{0.4}[1 + (5/6)\theta^{2.6} + (25/24)\theta^{5.2} - (1/3)\theta^{6.5} + 1.447\theta^{7.8} - (5/6)\theta^{9.1} + \cdots]. \tag{32}$$

Integration gives

$$(x/a)_0^\theta = 1.0514\theta^{1.4} + 0.3067\theta^4 + 0.2323\theta^{6.6} - 0.0621\theta^{7.9} + 0.231\theta^{9.2} - 0.117\theta^{10.5} + \cdots. \tag{33}$$

When $\theta \geqq 0.6$ Eq. (31) gives

$$1/\phi = 0.5064[1 + 0.6167Z + 0.0941Z^2 - 0.1809Z^3 - 0.227Z^4 - 0.172Z^5 + \cdots]/Z. \tag{34}$$

Integrating we obtain the indefinite integral, and find the integration constant by comparison with Eq. (33) at $\theta = 0.6$, where both series are sufficiently convergent to give results accurate to 1 part in 1,000

$$(x/a)_0^{1-z} = 0.2247 - 1.1660 \log_{10} Z - 0.3123Z - 0.0238Z^2 + 0.0305Z^3 + 0.0287Z^4 + 0.0174Z^5 + \cdots. \tag{35}$$

Column 2, Table II was calculated from Eqs. (33) and (35).

Lead-filament junction temperature. The rate of flow of heat, Q, in watts, past any point of the filament is equal to the integral, from that part to the center, of the difference between the heat generated by resistance and that lost by radiation.

$$Q = w_m a \int_\theta^1 (\theta^{1.2} - \theta^{5.1}) d\theta/\phi. \tag{36}$$

Setting $w_m = Av_m$, substituting for a from Eq. (28), and integrating

$$Q = (1.812 \cdot 10^{-5} T_m^{1.3}) 6.5^{-0.5} (3 - 5\theta^{2.6} + 2\theta^{6.5})^{0.5} A \tag{37}$$

where θ corresponds to the temperature of the point in question.

For short fairly heavy leads at temperatures below 1,000°K the resistance loss and radiation loss in the lead are negligible. All the heat that flows into the lead from the filament must flow out at the cold end, which may be assumed to be at room temperature. Taking the heat conductivity of nickel leads as constant at 0.586 watts cm^{-1} deg^{-1}, the leads have a constant temperature gradient given by

$$\lambda_L(dT/dl)\pi D_L^2/4=Q. \tag{38}$$

Consequently for the total temperature difference $\Delta T=T_0-T_R$ for the leads we obtain

$$\Delta T=4lQ/(\pi D_L^2\lambda_L). \tag{39}$$

Eqs. (37) and (39) give Eq. (4b) for ΔT in terms of $(\Delta T)_0$. To find the latter we notice that the lead temperature θ_0 has little effect on Q. Setting $\theta_0=0.24$, $A=1, l=1$, $D_L=0.1$, $\lambda_L=0.586$, we obtain from Eqs. (37) and (39)

$$(\Delta T)_0=145[1.812\cdot 10^{-5}T_m^{1.3}]. \tag{40}$$

Eq. (40) was used in conjunction with Table V to compute Table III.

Filament characteristics. We have

$$2\Delta H=H_m-H=2a\int_{\theta_0}^{1}(h_m-h)d\theta/\phi. \tag{41}$$

Applying Eqs. (6) and (28) and substituting for h_m/v_m the equal ratio H_m/V_m, where V_m is the voltage drop that would exist between the ends of the filament if it were all at the temperature T_m

$$\Delta V_H=\Delta H(V_m/H_m)=1.812\cdot 10^{-5}T_m^{1.3}\int_{\theta_0}^{1}(1-\theta^n)d\theta/\phi. \tag{42}$$

ΔV_H is a convenient symbol for the expression $\Delta H(V_m/H_m)$. It represents the voltage across a section of uncooled filament of such length that H_m for this section would equal the decrease caused by the cooling effect of the lead. The advantage of this nomenclature is that it requires no knowledge of filament diameter or length.

By breaking up the integral of Eq. (42) into

$$B_1=\int_0^1(1-\theta^n)d\theta/\phi \tag{43}$$

and

$$\beta(\theta_0)=\int_0^{\theta_0}(1-\theta^n)d\theta/\phi \tag{44}$$

we obtain Eq. (12).

In evaluating B_1, we meet the difficulty that we must use two different series for $1/\phi$, one for small and the other for large values of θ. Let $1/\phi_1$

be the value of $1/\phi$ given by the first six terms only of the series in Eq. (32) and $1/\phi_2$ by the first six terms only of the series in Eq.(34). We have

$$\begin{aligned} 0 &\leqq \theta \leqq 0.5 && \phi = \phi_1 \\ 0.5 &< \theta < 0.65 && \phi_1 = \phi = \phi_2 \\ 0.65 &\leqq \theta \leqq 1 && \phi = \phi_2. \end{aligned}$$

Since the series are equivalent between 0.5 and 0.65 we may put

$$B_1 = \int_0^t (1-\theta^n)d\theta/\phi_1 + \int_t^1 (1-\theta^n)d\theta/\phi_2$$

where $0.5 < t < 0.65$. A simple transformation gives

$$B_1 = \int_0^t (1-\theta^n)(1/\phi_1 - 1/\phi_2)d\theta + \int_0^1 (1-\theta^n)d\theta/\phi_2. \tag{45}$$

The value of $1/\phi_1 - 1/\phi_2$ is practically zero for values of θ between 0.5 and 0.65, and therefore the value of the first integral is not dependent on the actual value of t. Even at $\theta = 0.1$ the value of $1/\phi_1 - 1/\phi_2$ is only 0.117, but at $\theta = 0$ it becomes 0.573. Thus the larger part of the first integral is for values of $\theta < 0.1$. In this range θ^n may be neglected in comparison with unity for all large values of n. Even if $n = 1$ the error in neglecting θ^n will be small.

Calling the first integral of Eq. (45) F_1, we have

$$\begin{aligned} F_1 &= \int_0^t d\theta/\phi_1 - \int_0^t d\theta/\phi_2 \\ &= (x/a)_0^t - \int_0^t d\theta/\phi_2. \end{aligned} \tag{46}$$

Designate the right hand side of Eq. (35) by F_2. From the derivation of this equation

$$F_2 + C = \int d\theta/\phi_2$$

C being a constant of integration. Hence

$$\int_0^t d\theta/\phi_2 = [F_2+C]_{\theta=0}^{\theta=t} = [F_2+C]_{z=1}^{z=1-t} = F_2(1-t) - F_2(1).$$

But from Eq. (35) $F_2(1-t) = (x/a)_0^t$. Hence from Eq. (46)

$$F_1 = F_2(1) = -0.0348$$

the numerical value being found by setting $z = 1$ in the expression for F_2 in Eq. (35). Due to the definition of ϕ_2 this value is not affected by the missing terms of the series.

Putting the value of $1/\phi_2$ from Eq. (34) in the second integral of Eq. (45), we find

$$B_1 = -0.0348 + 0.5064 \sum_{p=1}^{6} A_p \int_0^1 (1-\theta^n)(1-\theta)^{p-2} d\theta$$

where A_1, A_2, A_3 are the coefficients, 1, 0.6167, etc., in the series in Eq. (34). This reduces to

$$B_1 = 0.2247 + 0.5064 \int_0^1 (1-\theta^n) d\theta/(1-\theta) - 0.3123/(n+1)$$
$$-0.0477[(n+1)(n+2)]^{-1} + 0.1833[(n+1)\cdots(n+3)]^{-1}\cdots \quad (47)$$

the coefficients of the next two terms being 0.6894 and 2.092.

If n is an integer we have

$$\int_0^1 (1-\theta^n) d\theta/(1-\theta) = 1 + \tfrac{1}{2} + \tfrac{1}{3} + \tfrac{1}{4} + \cdots + 1/n \quad (48)$$

and for other values of n the integral can be expressed in terms of gamma functions. For $n = 1.2$, its value is 1.1216. For large values of n the integral is given by the series

$$\int_0^1 (1-\theta^n) d\theta/(1-\theta) = 0.5772 + \log_e n + 1/2n$$
$$-[12n(n+1)]^{-1} - [12n(n+1)(n+2)]^{-1}. \quad (49)$$

Inserting this value in Eq. (47) and expressing as a series in reciprocal powers of n we obtain Eq. (13).

In computing Table IV for values of n less than 5, Eq. (47) was used but Eq.(13) was found more convenient for the larger values.

To evaluate $\beta(\theta_0)$ we note that in general $\theta_0 < 0.5$ and hence that for fairly large n the term θ^n is negligible, and Eq. (14) holds. For ΔV, when $n = 1.2$, $\beta(\theta_0)$ for the third column of Table II was obtained by using the series expansions of $1/\phi$ given by Eqs. (32) and (34).

Application under other conditions. For filaments in the presence of gas, or for filaments of materials other than tungsten there will be changes in the values used in Eq. (29) for ω, ρ and k, where k is the temperature exponent of the thermal conductivity. By methods similar to the derivation of Eq. (30) we find that the general expression for ϕ is

$$\phi^2 = 2\theta^{-2k}[(1-\theta^{\rho+k+1})/(\rho+k+1) - (1-\theta^{\omega+k+1})/(\omega+k+1)]. \quad (30a)$$

The integral B_1 in Eq. (12) may be found by numerical integration or by direct integration in some cases. Thus, when $\omega+k+1 = 2(\rho+k+1)$, ϕ^2 is a perfect square, and

$$B_1 = (\omega-\rho)^{-1/2}\{\psi[(n+k+1)/(\rho+k+1)] - \psi[(k+1)/(\rho+k+1)]\} \quad (50)$$

where $\psi(x) = d\ln\Gamma x/dx$ is the logarithmic derivative of the gamma function. Table IVa gives some values of B_1 obtained in some of these ways.

TABLE IVa.
$B_1=\int_0^1(1-\theta^n)d\theta/\phi$ for various exponents ω, ρ, k, n

ω	ρ	k	n	B_1
5.1	0.0	1.0	5.1	1.695
4.3	1.85	−.4	20.	4.079
6.0	1.0	1.0	1.0	0.371
4.0	1.0	1.0	1.0	0.428
4.0	1.0	1.0	5.0	1.118
4.0	1.0	1.0	10.0	1.486
4.0	1.0	1.0	20.0	1.871
4.0	1.0	1.0	40.0	2.264
3.8	1.2	0.4	27.2	2.522

Data such as those in Table IVa show that the variation of B_1 with ω is small and may be represented thus

For $n=\rho$ $$B_1=B_{15}[1+0.077(5.0-\omega)] \tag{51a}$$

For $n=20$ $$B_1=B_{15}[1+0.100(5.0-\omega)] \tag{51b}$$

where B_{15} is the value of B_1 for $\omega=5.0$. B_{15} may be found by these equations from tables of B_1 such as Table IVa. Fig. 1 is a plot of B_{15} as abscissa against ρ as ordinate for constant values of k. The full lines are for voltage correction, $n=\rho$. The dotted lines are for $n=20$.

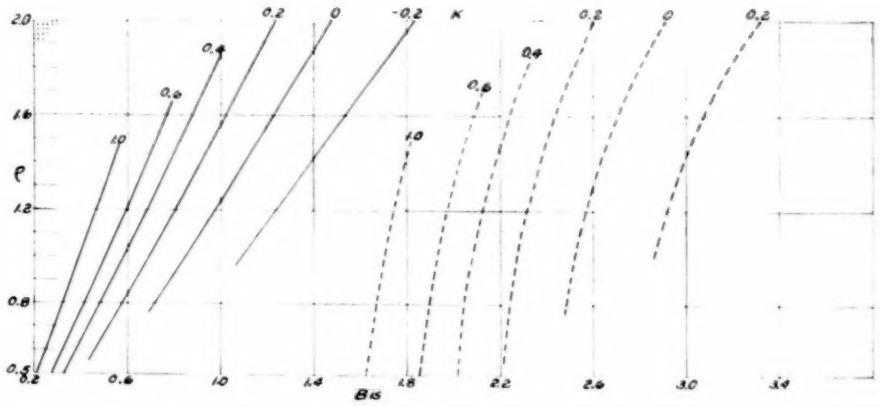

Fig. 1. Plot of B_{15} ($\omega=5$) against ρ for constant k.
Full lines $n=\rho$. Dotted lines $n=20$.

The deviations of B_1 found from Fig. 1 from the value of B_1, for the same n, found in Table IV may be expressed as a fraction, N, of the latter value. The variation of N with n, for constant values of ω, ρ and k may be approximately expressed by

$$N(n)=N(20)-\alpha(20-n)[N(20)-N(\rho)]/(20-\rho) \tag{51c}$$

where

n / ρ	5	10	30	40
α 1	0.42	0.27	0.15	0.11

We may find B_1 for any exponents n, ω, k and ρ by finding $N(20)$ and $N(\rho)$ for the appropriate values of ω, k and ρ from Fig. 1 and Eqs. (51a) and (51b). Eq. (51c) and Table IV then give the desired B_1.

Other metals. From Eq. (26) and the derivation of Eq. (28) we see that

$$a=(\lambda_m T_m R_m/v_m)^{1/2} \tag{28a}$$

where R_m is the resistivity of the metal in question at the temperature T_m. We then have

$$\Delta V_H=(\lambda_m T_m R_m)^{1/2}[B_1-\beta(\theta_0)]. \tag{12a}$$

The Wiedemann-Franz law states that, at a given temperature, λR, and hence the coefficient in Eq. (12a), is approximately the same for most metals and alloys. This coefficient is thus given by $1.812\cdot 10^{-5}T_m^{1.3}$ in Table V. Consequently the magnitude of ΔV_H may be found for any metal which obeys this law with the help of Fig. 1 and the assumption that the change of $\beta(\theta_0)$ is similar to that of B_1.

End losses from filaments in the presence of gas. Gas around a filament causes a loss of heat by conduction and increases the voltage required to reach a given T_m. Eq (12a) shows that for a fixed T_m, ΔV_H is the same for filaments in gas and vacuum except for the variation in the values of B_1 and $\beta(\theta_0)$. The latter may be eva'uated by considering the conduction loss to be part of the radiation loss w in Eq. (23). Thus if at T_m the conduction loss is 1/4 of the radiation loss, and if the conduction loss varies as $T^{1.7}$,[17] the effect on B_1 may be represented as a change in the effective value of ω from 4.6 to 3.8, which by Table IVa means an increase of about 15 percent in the values of B_1 given in Table IV. In general the values of ΔV_H for vacuum hold with fair accuracy for small gas pressures, but the temperature distribution is altered.

For new filament materials or other new conditions there will be no accurate knowledge of the filament characteristics and the temperature exponents for the application of the above method, which method nevertheless will, we hope, still be capable of indicating whether or not lead losses are important in any given case.

Part II. Lead Losses in Short Filaments

Temperature distribution. Shorter filaments do not admit the assumption, made for most of the results of Part I, that the central portion of the filament is not cooled by the leads. Even the calculation of temperature distribution by adding the effects of the two leads is not very good in these cases. Thus when x/a, the filament half length, is 1.53, for which the cooling effect of one lead at the other gives $\theta=0.994$, the long filament case gives a central temperature corresponding to $\theta=0.85$, while the true value is $\theta=0.8$. Theoretically the maximum temperature T_m can only be attained in an infinitely

[17] These conditions are approximately those for a filament of 0.007 cm diameter at $T_m=2900°$ in 10 mm of N_2. See I. Langmuir and G. M. J. Mackay, J. Amer. Chem. Soc. **36**, 1717 (1914). For larger filaments the conduction losses are relatively smaller.

long filament (cf. Eq. (35)). A "short filament" is one for which this fact invalidates the conclusions of Part I.

Let T_c be the actual temperature at the center of the filament, and let the larger value T_m still indicate the temperature of a hypothetical portion uncooled by leads as calculated from the current and diameter of the filament. Let $\theta_c = T_c/T_m$.

Eq. (1) holds as before with a more complicated value for ϕ. If $(x)_{\theta_0}^{\theta_c}$ is the distance from the center to a lead at temperature $T_0 = \theta_0 T_m$, we have, as before

$$(x/a)_{\theta_0}^{\theta_c} = \int_{\theta_0}^{\theta_c} d\theta/\phi \tag{52}$$

a has the same values as before, and is given in Table I.

Table IX gives the values of $(x/a)_0^{\theta_c}$ for various values of θ_c. Fig. 2 gives the plot of $(x/a)_\theta^{\theta_c}$ as abscissa against θ as ordinate, for constant values of θ_c. The value of θ_c for any curve is of course the intercept on the θ axis.

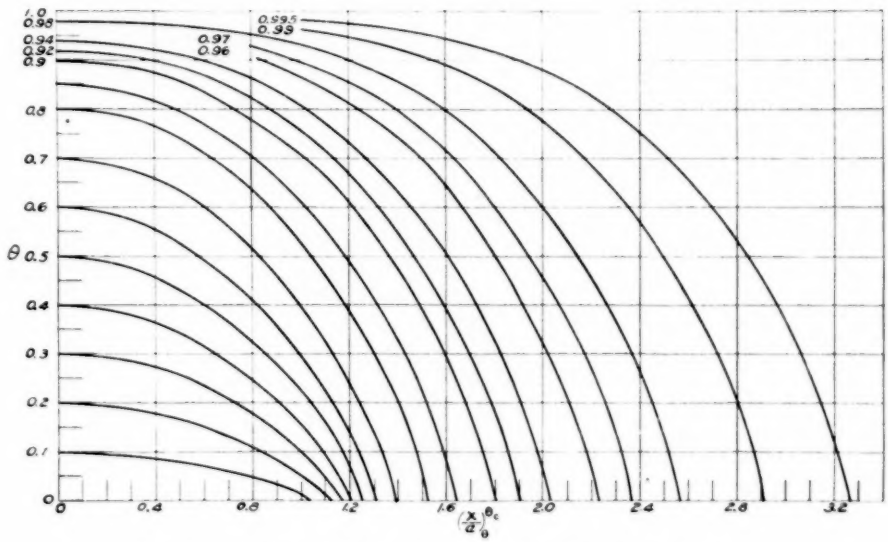

Fig. 2. Plot of $(x/a)_\theta^{\theta_c}$ against θ for constant values of θ_c.

These curves are temperature distribution curves. Thus if $\theta_c = 0.8$ the curve with that intercept gives us the temperature (θ) at any distance, $(x/a)_\theta^{\theta_c}$, from the center. To find for any filament the value of θ_c, we need know only one point on the temperature distribution curve. Thus for a filament of known length and of known lead temperature, a point having the coordinates $(x/a)_{\theta_0}^{\theta_c}$, θ_0 is determined on the plot. This point lies on some temperature distribution (constant θ_c) curve—probably not one of these drawn. The value of θ_c may readily be found, however, by interpolating between the two nearest curves. By continuing this interpolation down to the x/a scale, the value $(x/a)_0^{\theta_c}$ is found. This is the value that would obtain if the given

filament were prolonged until its leads were at 0°K, and were left otherwise unchanged. If desired, $(x/a)_0^{\theta_c}$ may be found from θ_c by interpolating in Table IX.

Of course the value of any property h at any point of the filament may be found by first finding the temperature at that point, then applying published data on filament characteristics.[1,3]

TABLE IX. *Relation between the temperature $T_c=\theta_c T_m$ at the center of a short filament with leads at °K and the length $(2x)$ of the filament.*

θ_c	$(x/a)_0^{\theta_c}$	θ_c	$(x/a)_0^{\theta_c}$	θ_c	$(x/a)_0^{\theta_c}$
0.005	0.7325	0.4	1.2065	0.94	2.031
.01	.8262	.5	1.2510	.95	2.118
.03	.9221	.6	1.3077	.96	2.225
.05	.9704	.7	1.3905	.97	2.365
.1	1.0401	.8	1.5280	.98	2.565
.2	1.1154	.85	1.6399	.99	2.912
.3	1.1645	.9	1.802	.995	3.261
		.92	1.899	.999	4.074

The effect of lead losses on characteristics. If all the filament were at the actual maximum temperature, T_c, the value H_c of any property for the whole filament would be

$$H_c = 2h_c x = 2ah_c(x/a)_{\theta_0}^{\theta_c}. \tag{53}$$

h_c is the value of the property in question for 1 cm of filament at temperature T_c. The ratio of the actual value for the whole filament, H, to the hypothetical value is H/H_c. The value of this ratio when $\theta_0=0$ we designate as $(H/H_c)_0$. If $n>4$, H is independent of θ_0 for constant θ_c for all the practical range. Hence, applying Eq. (53)

$$H = 2ah_c(x/a)_0^{\theta_c}(H/H_c)_0. \tag{54}$$

H, and hence H/H_c, is a function of n, the temperature exponent of the property in question. In Fig. 3, ordinates $(H/H_c)_0$ are plotted against abscissae $(x/a)_0^{\theta_c}$ for constant values of n (the full lines). The scale for $(x/a)_0^{\theta_c}$ at the top, and the scale for θ_c on the bottom may be used interchangeably. They correspond as in Table IX.

For a given filament, knowing x, a, and θ_0, $(x/a)_0^{\theta_c}$ is determined from Fig. 2. Fig. 3 then yields $(H/H_c)_0$ for the value of n corresponding to the property in question. H may then be found from Eq. (54).

For $n \leqq 4$, H is not independent of θ_0. For $n=1.2$, the resistance-exponent, the dotted lines at the top of Fig. 3 give the value of H/H_c [*not* $(H/H_c)_0$] for constant values of $\tau_0=\theta_0/\theta_c$. Note however that this is still given in terms of the abscissa $(x/a)_0^{\theta_c}$.

For values of x/a less than 1.0, and hence not in Fig. 2, H/H_c is constant at the value for $x/a=1.0$.

It is to be remarked that for $T_c<1000$°K none of the given data apply accurately, nor is the temperature distribution accurate. This is because of the uncertainty in the value of λ here.

Limits of long filament case. Table X gives the smallest value of $(x/a)_0^{\theta_c}$ for which the errors in H/H_c made in applying the long filament instead of the short filament case are less than the percentage at the head of the column. The errors of course depend somewhat on the value of n for the property under consideration. A (+) after the value of n indicates that the long filament case gives too large a value of H/H_c, or of H; that is, too

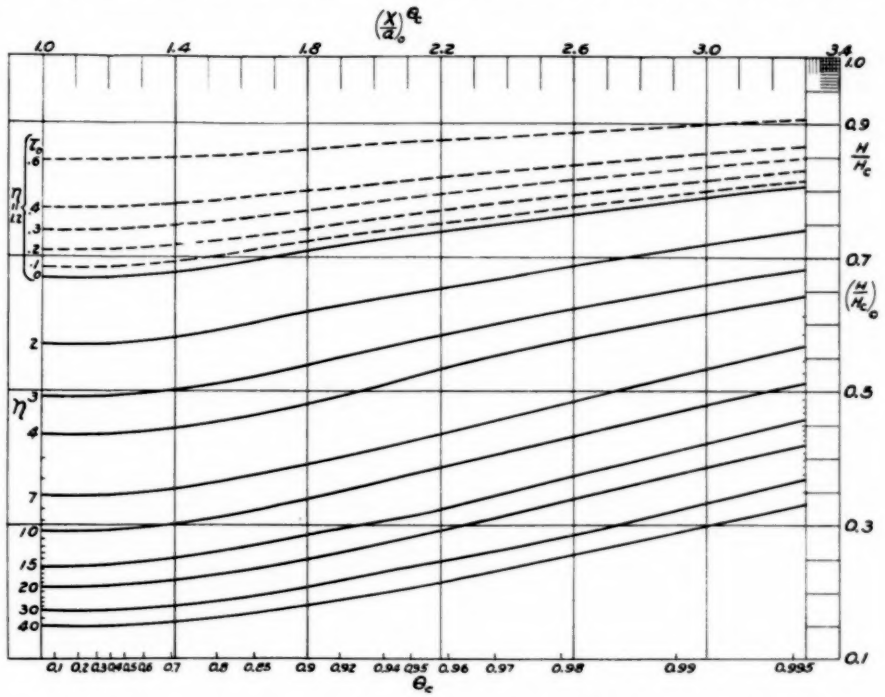

Fig. 3. Full lines $(H/H_c)_0$ for constant n against $(x/a)_0^{\theta_c}$ and θ_c. Dotted lines H/H_c for $n=1.2$ constant τ_0 against $(x/a)_0^{\theta_c}$ and θ_c.

small a value of B_1. In the neighborhood of $n=5$ the sign of the error changes. For $n=1$ (temperature distribution) the long filament case gives too high temperatures, even when the cooling effects of the two leads are added.

Lead temperatures may be found with sufficient accuracy for most cases from Table III of Part I. For high accuracy or for very short filaments Eqs. (36) and (39) may be applied directly, using Eq. (55).

TABLE X. *Errors in H/H_c made in assuming a filament to come under Part I. This able gives approximately the smallest value of $(x/a)_0^{\theta_c}$ for which the error made by that assumption is less than the percentage given at the head of the column.*

n	1 percent	5 percent	n	1 percent	5 percent
1.0(+)	1.9	1.6	10(−)	2.8	2.3
1.2(+)	1.9	1.7	15(−)	2.9	2.6
4(+)	1.9	1.8	20(−)	3.0	2.7
5(±)	1.6	1.6	30(−)	3.2	3.0
7(−)	2.3	2.0	40(−)	3.3	3.0

Computation of temperature distribution. Eq. (30) holds with a new constant of integration determined by the condition $\phi = ad\theta/dx = 0$ when $\theta = \theta_c$ (the maximum temperature):

$$1.3\phi^2 = \theta^{-0.5}(\theta_c^{2.6} - 0.4\theta_c^{6.5} - \theta^{2.6} + 0.4\theta^{6.5}). \tag{55}$$

The integration in Eq. (52) is best carried out by series approximations.
Case I. $\tau = \theta/\theta_c$ is small

$$(x/a)_0^\theta = \theta_c \int_0^t d\tau/\phi. \tag{56}$$

Expressing Eq. (55) in terms of τ, then expanding $1/\phi$ by the binomial theorem and integrating the resulting series term by term

$$(x/a)_0^\theta = 0.8144A^{0.5}\theta_c^{0.1}\tau^{1.4}[1 + 0.175A\tau^{2.6} + 0.0795A^2\tau^{5.2} - 0.0354A\theta_c^{3.9}\tau^{6.5} + \cdots] \tag{57}$$

where $A = 1/(1 - 0.4\,\theta_c^{3.9})$.

In Eq. (57) $\tau^{9.2}$ has been neglected. If $\theta \leqq 0.6\,\theta_c$ the error is less than 1 percent. If in this series we set $\theta_c = 1$, we get the series of Eq. (33) of Part I.
Case II. $\sigma = 1 - \tau = (\theta_c - \theta)/\theta_c$ is small and θ_c is also small.

Eq. (55) may be expanded in terms of σ to give

$$\phi^2 = 2\theta_c^{1.8}\sigma(1 - \theta_c^{3.9})(1 - \sigma)^{-0.8}[1 - 0.8\sigma(1 - 2.438\theta_c^{3.9}) + 0.16\sigma^2(1 - 24.78\theta_c^{3.9}) + 0.016\sigma^3(1 + 229\theta_c^{3.9}) + \cdots].$$

Terms of the form $(1 - b\theta_c^{3.9})/(1 - \theta_c^{3.9})$ were expanded by the binomial theorem, and $\theta_c^{7.8}$ and higher powers neglected. Expanding $1/\phi$ and integrating

$$(x/a)_\theta^{\theta_c} = \theta_c \int_0^\sigma d\sigma/\phi = \theta_c^{0.1}(1 + \tfrac{1}{2}\theta_c^{3.9})(2\sigma)^{0.5}[1 - 0.33\theta_c^{3.9}\sigma - 0.024\sigma^2(1 - 10\theta_c^{3.9}) - 0.0034\sigma^3(1 + 5.38\theta_c^{3.9})]. \tag{58}$$

This is accurate when σ^4 and $\theta_c^{7.8}$ may be neglected in comparison with unity. At $\theta_c = 0.56$ this error is about 1 percent.
Case III. σ is small and θ_c large.

Let $z = 1 - \theta$ and $z_c = 1 - \theta_c$. z and z_c are both small. Expanding (55) by the binomial theorem

$$1/\phi = 0.5064(1 - 0.4z - 0.12z^2 + \cdots)(z^2 - z_c^2)^{-0.5}[1 + 1.0167C_1 + C_2 + \cdots]. \tag{59}$$

where

$$C_1 = (z^3 - z_c^3)/(z^2 - z_c^2) \doteq z[1 + (1/2)(z_c/z)^2]$$

$$C_2 = 1.5504C_1^2 - 0.930(z^4 - z_c^4)/(z^2 - z_c^2) \doteq [0.621 + 1.008(z_c/z)^2]z^2$$

substituting, multiplying Eq. (59) out, collecting like terms and integrating

$$(x/a)_{\theta}^{\theta_c} = \int_{z_c}^{z} dz/\phi = 0.5064(1+0.852z_c^2) \text{ arc cosh } (z/z_c) + 0.3123(z^2-z_c^2)^{0.5} + 0.2574z_c \text{ arc cos } (z_c/z) + 0.0239z(z^2-z_c^2)^{0.5} \quad (60)$$

This series is good if $\theta_c \geqq -0.7$; $\theta \geqq 0.5$.

Case IV. θ_c is nearly unity.

We may choose z small enough for series (60) to converge, but at the same time much larger than z_c. The small quantity z_c then has little effect on the integral from 0 to $1-z$. To evaluate this integral we may neglect z_c entirely and use Eq. (35) of the long filament case, which, by the choice of the integration constant, gives the value of $(x/a)_0^{\theta}$. z as chosen above is sufficiently small for this series also to converge. Adding Eqs. (35) and (60), expressing arc cosh (z/z_c) as a logarithm and arc cos (z_c/z) as a series, and remembering that z is much larger than z_c, we obtain

$$(x/a)_0^{\theta_c} = 0.5757 - 1.16596 \log_{10} z_c + 0.4043z_c + 1.9z_c^2. \quad (61)$$

The coefficient of the last term was chosen empirically so as to compensate for the missing terms. Note that the result is independent of the specific value of z, as long as it has such a value as to make the derivation valid.

Thus we can obtain $(x/a)_0^{\theta}$ by Case I and $(x/a)_{\theta}^{\theta_c}$ by Case II or III. These two methods overlap in the admissible values of θ except for intermediate values of θ_c, when neither Case II nor Case III is very good. Numerical integration was used for accurate results in this region. The value of $(x/a)_0^{\theta_c}$ may be obtained by Case IV or by the formula

$$(x/a)_0^{\theta_c} = (x/a)_0^{\theta} + (x/a)_{\theta}^{\theta_c}.$$

Table VII and Fig. 2 were obtained by the above methods.

Filament characteristics. Assuming as in Part I that the value of the property in question varies as the nth power of the temperature, we have

$$H = 2h_c \int_0^x (T/T_c)^n dx = 2ah_cJ \quad (62)$$

where

$$J = (1/\theta_c^n) \int_0^{\theta_c} \theta^n d\theta/\phi - (1/\theta_c^n) \int_0^{\theta_0} \theta^n d\theta/\phi. \quad (63)$$

If $n > 4$, θ^n becomes rapidly smaller with decreasing θ. Hence we may neglect the second integral to obtain

$$J = (1/\theta_c^n) \int_0^{\theta_c} \theta^n d\theta/\phi. \quad (64)$$

From Eqs. (53) and (62)

$$(H/H_c)_0 = J/(x/a)_0^{\theta_c}. \quad (65)$$

There are two limiting cases to be considered.

Case I. θ_c is small.

We may neglect $\theta_c^{6.5}$ in Eq. (55). Introducing $\tau=\theta/\theta_c$ we obtain from Eqs. (63), (53), (62), (52), and (55)

$$H/H_c=\frac{\int_{\tau_0}^{1}\tau^{n+0.4}d\tau(1-\tau^{2.6})^{-0.5}}{\int_{\tau_0}^{1}\tau^{0.4}d\tau(1-\tau^{2.6})^{-0.5}}.$$

The value of θ_c has cancelled out. If $\tau_0=\theta_0/\theta_c$ is held fixed, then H/H_c is independent of θ_c. Hence in Fig. 3 the values for $x/a<1.0$ are the same as those given for $x/a=1.0$.

Case II. θ_c is large.

As θ_c approaches unity we get the transition from the short filament to the long filament case. When $z_c=1-\theta_c$ can be neglected entirely, Eqs. (64) and (43) give

$$(x/a)_0^{\theta_c}-\theta_c{}^nJ=B_1. \tag{66}$$

From Eq. (62)

$$H=2ah_m(\theta_c{}^nJ).$$

Thus when (66) is satisfied the value of H increases in direct proportion to the increase of length. This is because the central portion, to which the increased length is added, is at practically constant temperature.

The degree to which Eq. (66) is satisfied is a measure of the approximation involved in assuming that the filament is long. To construct Table VIII the true values of J as found below were compared with the value calculated from Eq. (66). For $n=0$ the short filament temperature distributions were compared with those obtained from the long filament case by adding the cooling effect of the two leads.

Evaluation of J. If θ_c and hence $D=0.4\,\theta_c^{3.9}\,(1-0.4\,\theta_c^{3.9})^{-1}$ is small, we set $y=(\theta/\theta_c)^{2.6}$ in Eq. (64) and obtain, using Eq. (55)

$$J=\theta_c^{0.1}M(1/5.2)^{1/2}(1-0.4\theta_c^{3.9})^{-1/2} \tag{67}$$

where

$$M=\int_0^1 y^p dy(1-y)^{-1/2}[1-Dy(1-y^{3/2})(1-y)^{-1}]^{-1/2} \tag{68}$$

and $n=2.6p+1.2$. M may be expanded as a power series in D

$$M=G_0+(1/2)G_1D+(3/8)G_2D^2+(5/16)G_3D^3+\cdots \tag{69}$$

where

$$G_k=\int_0^1 y^{p+k}(1-y)^{-1/2}[(1-y^{3/2})(1-y)^{-1}]^k dy. \tag{70}$$

Each of these integrals may be expanded in terms of $u=1-y$, and then integrated by means of gamma functions.

$$G_0=\pi(-1/2)\pi(p)/\pi(p+1/2) \tag{71}$$

$$G_1=\frac{3\pi(-1/2)\pi(p+1)}{2\pi(p+3/2)}[1-(1/8)(p+5/2)^{-1}$$
$$-(1/32)(p+5/2)^{-1}(p+7/2)^{-1}+\cdots]$$

$$G_2=\frac{9\pi(-1/2)\pi(p+2)}{4\pi(p+5/2)}[1-(1/4)(p+7/2)^{-1}$$
$$-(1/64)(p+7/2)^{-1}(p+9/2)^{-1}+\cdots]$$

$$G_3=\frac{27\pi(-1/2)\pi(p+3)}{8\pi(p+7/2)}[1-(3/8)(p+9/2)^{-1}$$
$$+(3/64)(p+9/2)^{-1}(p+11/2)^{-1}+\cdots].$$

As θ_c and D become larger the series of Eq. (69) does not converge rapidly. A better series may be obtained by setting

$$M=G_0(1-g_1D-g_2D^2-\cdots)^{-1/2} \tag{72}$$

and determining the value of each g_i in terms of the G_k's by expanding Eq. (72) and equating coefficients with Eq. (69).

If θ_c is very small, D may be neglected entirely. For the case $n=0$, Eqs. (69), (71), (67) give

$$J=(x/a)_0^{\theta_c}=1.309(\theta_c)^{0.1}. \tag{73}$$

This is useful in determining the smaller values of Table VII.

When $0.9\leqq\theta_c<1$ even series (72) does not give accurate results. The values of J here were determined by means of Simpson's rule. The difficulties due to the infinite integrand at $\theta=\theta_c$ were avoided by an integration by parts.

If n is small, θ_o may not be neglected as in Eq. (64). The most important case is $n=1.2$ (the exponent for resistance). The values of J may be found from Eq. (63), the first integral being evaluated by the methods above, and the second integral by a series similar to that of Eq. (57). This holds over the useful range $\theta_0\leqq 0.6\ \theta_c$.

A similar method might be used for other small values of n. The calculations for the second integral may be simplified by neglecting $\theta^{6.5}$ in Eq. (55). At $\theta_0=0.6\theta_c$ the error made thus is less than 3 percent for any short filament ($\theta_c\leqq 0.94$). Since this integral is a correction term, the approximation is justified. By substituting $u=1-0.4\theta_c^{3.9}-(\theta/\theta_c)^{2.6}$, the integral is reduced to a form which may be evaluated in terms of elementary functions for $n=1.2$, 2.5, 3.8, 5.1 and 6.4. Interpolation may be used for intermediate values of n.

For $n\geqq 4$ Eq. (64) is valid, unless high accuracy is desired. When $n=10$, $\theta_c=0.7$, $\theta_0=0.5$, the error is less than 1 percent.

Experimental checks. Several lamps were made up to test the short filament theory by experiment. Filament L was a straight filament 1.6 cm long, $D=0.0256$ cm, cut from a length of wire that had been aged 24 hours at 2400°. It was welded to nickel leads 5 cm long, $D_L=0.254$ cm. The temperature distribution along this filament was measured by means of an optical pyrometer mounted on a carriage that could be moved along a horizontal scale which gave the position of the pyrometer accurately to 0.001 inch. The pyrometer had previously been calibrated against a standard lamp.

The curves in Fig. 4 show the temperature distribution for three different currents. The solid lines indicate the observed values, and a comparison of T_c in each case with the corresponding value of T_m listed in the corner of

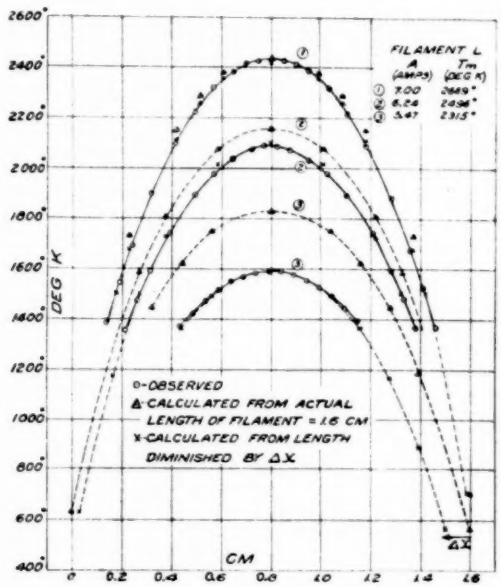

Fig. 4. Temperature distribution for filament L, $D=0.0256$ cm, $2x=1.6$ cm, wire aged throughout its length. Experimental and theoretical curves.

the graph, shows that the center of the filament is greatly cooled by the leads; in other words, filament L is a "short filament."

The temperature distribution was calculated from the short filament theory and the results shown in the curves marked by triangles. In Curve 1 where $\theta_c=0.912$ and $T_m-T_c=234°$, the agreement with experiment is fairly good. In the more nearly extreme cases of Curve 2 where $\theta_c=0.836$, $T_m-T_c=408°$, and Curve 3 where $\theta_c=0.687$, $T_m-T_c=725°$, the temperatures given by the theory are too high. We attribute this departure from the observed values to an error in the value of λ at the cool ends of the filament. The heat conductivity of tungsten is not accurately known at temperatures below incandescence, and if we have used values of λ in this range that are too low, so that the calculated temperature gradient near the leads is too steep, the resulting T_c will be too high. An error from this source becomes important

only when the short filament theory is put to the severe test of predicting T_c in cases where T_c is much less than T_m.

Since T_c must be known before either the voltage or the candle-power of a filament can be calculated, the following empirical addition to the theory has been devised, to be used in those cases in which T_c can be determined only by calculation. To compensate for the error that results from using values of λ that are too low, we proceed as if the length of the filament were shortened by an amount Δx such that the heat loss by conduction will be increased above Q_λ, the value corresponding to λ, by an amount $\psi = 4Q_\lambda \Delta x/(\pi D^2)$. Q_λ is given by Eq. (37) which for $\theta_0 = 0.24$ becomes approximately

$$Q_\lambda = 0.6654\, A\, \theta_c (1.812 \cdot 10^{-5} T_m^{1.3}) \tag{74}$$

It has already been pointed out, in connection with the derivation of Eq. (40), that changes in θ_0 have little effect on the factor 0.6654. θ_c supplies approximately the factor by which Q_λ must be reduced when the integration in Eq. (36) is carried only to θ_c instead of to 1. The term in brackets is given in Tab'e V. Values of ψ derived from the data of Fig. 4 are given in Table XI. They were calculated using those values of Δx which made the theoretical and observed curves coincide at 1500°; the theoretical curves are indicated by crosses. ψ is tabulated as a function of T_0, since the error is greater at low lead temperatures.

TABLE XI.

$T_0 =$	300°	400°	500°	600°
$\psi =$	471	367	263	159

From Table V and Table XI one can calculate

$$\Delta x = \pi D^2 \psi/(4Q_\lambda) \tag{75}$$

and subtract Δx from the actual half length x of the filament before calculating T_c. This correction applies to calculations of T_c *only*, and the maximum values to be used are $0.15x$ for leads in air, and $0.22x$ for leads in liquid air.

Fig. 5 is a plot of the volt-ampere characteristics of filament G, 1.928 cm in length, $D = 0.0103$ cm. The curves labelled air, using the bottom scale for voltage are for the bulb at room temperature, 300°K. The curves labelled liquid air, using the top scale for voltage, are for the bulb immersed in liquid air.

The course of the liquid air observations for low voltages is interesting. For $450° < T_c < 1200°$ and $T_m \doteq 2{,}000°$, the current decreases with increasing voltage. This phenomenon has been obtained with all short filaments which have been tried in liquid air.

Thus for one value of the current there are in some cases three possible values of the central temperature of the filament. With a low temperature the heat generated is small and so the small temperature gradient is sufficient to carry away the heat and maintain equilibrium. Likewise, with a

higher central temperature the heat generated is greater and the larger temperature gradient is necessary to preserve stability. Hence it is possible that all three central temperatures may be stable. The phenomenon may be explained in more detail by assuming that below 1,200° λ is larger than the value given by Eq. (24). Analysis shows that the general form of Eq. (73), which gives $(x/a)_0^{\theta_c}$ for small θ_c, is

$$(x/a)_0^{\theta_c} \propto \theta_c^{(1+k-\rho)/2}. \tag{73a}$$

If k, the thermal conductivity exponent, is less than 0.2, then by Eq. (73a) the temperature distribution curves of Fig. 2 will cross near $\theta=0$ and $x/a=1$. Thus $(x/a)_0^{\theta_c}$ and hence also T_m and A decrease with increasing θ_c for small values of the latter. This is essentially the phenomenon observed above.

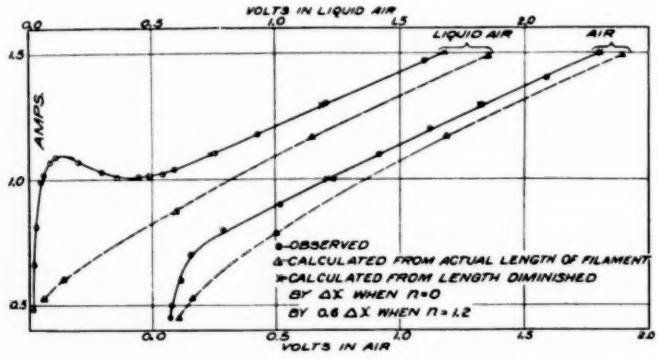

Fig. 5. Volt-ampere characteristics of filament G, $D=0.0103$ cm, $2x=1.928$ cm, wire aged throughout its length. Experimental and theoretical curves.

To obtain the calculated voltages, marked by crosses on the curves in Fig. 5, a correction of $0.6\Delta x$ subtracted from x was found sufficient to compensate for the decreased voltage drop along the ends of the filament due to the lower temperature which we assume to exist in this region. Thus for $n=0$, (temperature distribution) the correction is Δx; for $n=1.2$ it is $0.6\Delta x$; and for higher values of n no correction is needed.

Example of the calculations. To illustrate the method of calculating lead losses, consider filament G running at a current of 1.295 amps. From $D=0.01030$ cm we find $D^{3/2}=0.001045$, $A/D^{3/2}=1239$, thence $T_m=2222°$[12]. Table I gives by interpolation $a_0=0.400$, whence, as $D^{1/2}=0.1015$ we find from Eq. (2) that $a=0.406$. To determine the lead junction temperature, we find in Table III that $(\Delta T)_0=59°$ and hence with $l=5$ cm and $D_L=0.254$ cm Eq. (4b) gives $\Delta T=59°$. Thus $T_0=359°$, and by interpolation in Table XI $\psi=410$. Table IV gives $(1.812\cdot 10^{-5}T_m^{1.3})=0.4064$, so that from Eq. (75) we have $\Delta x=0.100$ cm if we put $\theta_c=1$. The half-length $x=0.964$, therefore $x'=x-\Delta x=0.864$. Dividing by $a=0.406$ we have $(x'/a)_{\theta_0}^{\theta_c}=2.128$. Since $T_0=359^0$ we find θ_0 by dividing by T_m, and have $\theta_0=0.1616$. We then find

the point of coordinates 2.128, 0.1616 on Fig. 2, and drawing through it a curve parallel to the given curves we obtain the intercepts $\theta_c = 0.959$[18] and $(x'/a)_0^{\theta_c} = 2.220$. Multiplying θ_c by T_m we find $T_c = 2131°$.

Eq. (54) shows that the voltage of a short filament is given by

$$V = A(H/H_c)8x\rho_c/(\pi D^2) \tag{76}$$

ρ_c is the resistivity at T_c and is $61.12 \cdot 10^{-6}$ ohm cm[18]. To find H/H_c we must first obtain τ_0 by dividing 359° by T_c to obtain 0.168. From Fig. 3 for abscissa $(x'/a)_0^{\theta_c} = 2.220$ we find $H/H_c = 0.766$. We substitute for x in Eq. (76) the corrected value $x - 0.6\Delta x = 0.904$ and obtain $V = 1.315$ volts. The experimental value was $V = 1.330$.

To find the candle power we use Eq. (54) to give

$$\text{Candle power} = H_c = 2aDC_c'(H/H_c)_0(x/a)_0^{\theta_c} \tag{77}$$

C_c', the specific candle power of tungsten at T_c, is found to be 47.3 international candles cm^{-2}[18]. From Eq. (18) using T_c instead of T_m we find the effective value of n to be 12.53. From Fig. 3 for abscissa $(x'/a)_0^{\theta_c} = 2.220$ we then find $(H/H_c)_0 = 0.362$. $(x/a)_0^{\theta_c}$ is obtained from $(x'/a)_0^{\theta_c}$ by multiplying by $x/(x - \Delta x)$ to give 2.477. We thus obtain $H_c = 0.355$ international candles. We did not measure the candle power in this instance, but in other instances similar calculations of candle power gave results that were in good agreement with experimental values.

Discussion of experimental checks. In ordinary practice the ends of a filament are "unaged," that is, they can never be heated to the temperature which a filament must once have before the properties become those of "aged" tungsten. It is known[6] that heating tungsten wire for one minute to a temperature of about 1500° causes the cold resistance to be lowered 15 to 20 percent, and presumably the heat conductivity would be increased at the same time by about the same amount. The filaments used for experimental checks were made from wire that had been previously aged throughout its length, in order to obtain uniform results, for the properties of unaged wire vary from sample to sample and depend on the history of the filament. It has been shown that in the case of aged tungsten the heat conductivity at the cool ends of the filament is higher than the values used in the theory. But where the filament is unaged in this region, the heat conductivity is lower than in the case of the aged filament which tends to restore λ to the values used in the theory so that in general the short filament theory may be used without the correction Δx to calculate lead losses from filaments that are made in the ordinary way.

[18] Where θ_c comes out to be less than 0.95 it is well to substitute θ_c equal to the calculated value instead of unity in Eq. (74), and thus arrive at a second approximation for Δx from Eq. (75).

THE ABSORPTION COEFFICIENT FOR SLOW ELECTRONS IN CADMIUM AND ZINC VAPORS

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(Received January 27, 1930)

Abstract

The variation with the electron velocity of the absorption coefficient, α, or the effective collision cross-section has been measured in the vapors of cadmium and zinc and found to follow a curve of the type previously found for mercury. The cadmium curve has a maximum at about 40 volts, $\alpha=130$, and a minimum at about 25 volts, $\alpha=126$, followed by a steady rise with decreasing velocity to the limit of accurate measurements, 1 volt, $\alpha=700$. The zinc curve has a very flat maximum at about 50 volts, $\alpha=76$, a minimum at about 36 volts, $\alpha=74$, followed by a steady rise to $\alpha=500$ at 1 volt. The magnitudes of the maximums are in the order: Cd, $\alpha=130$; Zn, $\alpha=75$; and Hg, $\alpha=60$. Other related properties of these atoms, such as the molar refractivity and the critical potentials, show this same irregularity in order.

THE measurement of the absorption coefficient for electrons in the noble gases, Ar, Kr and Xe,[1] has shown that the shape of the curves obtained is the same for all three of these. Similar measurements in the vapors of the alkali metals[2] have shown that these elements also have a characteristic type of curve. Mercury has been studied by Brode,[3,7] Maxwell,[4] Beuthe,[5] and Jones.[6] All of these observers except Beuthe have found a curve with values of the absorption coefficient in excellent agreement. Cadmium and zinc were also studied at the same time with the first measurements of mercury.[3] These observations were shown by subsequent experiments[7] to be unreliable, due to secondary and reflected electrons which were present in the form of apparatus used for the first measurements.

The apparatus, Fig. 1, used for the measurements of cadmium and zinc was of the same design as that described in the measurements of mercury.[7] About half of the measurements in cadmium vapor were made with the apparatus used for the mercury measurements. The mean radius of the path was 15 mm and the final slit was 0.5 mm wide. The rest of the observations in cadmium were made with an apparatus in which the mean radius of the path was 10 mm and the width of the final slit 1.0 mm. All of the measurements in zinc were made with this same apparatus.

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The control of the temperatures, the neutralization of the earth's field, the deflecting magnetic field, and the arrangement of the electrical circuits was the same as previously described in the mercury[7] and alkali[2] metal

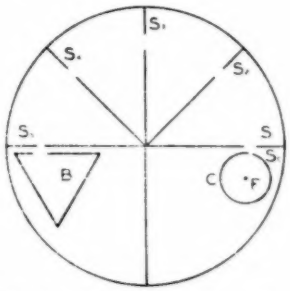

Fig. 1. Diagram of apparatus.

papers. The pressure of the gas was obtained from the vapor pressure at the temperature of the lower furnace which contained the supply of metal. This pressure was corrected for thermal effusion and the observations were

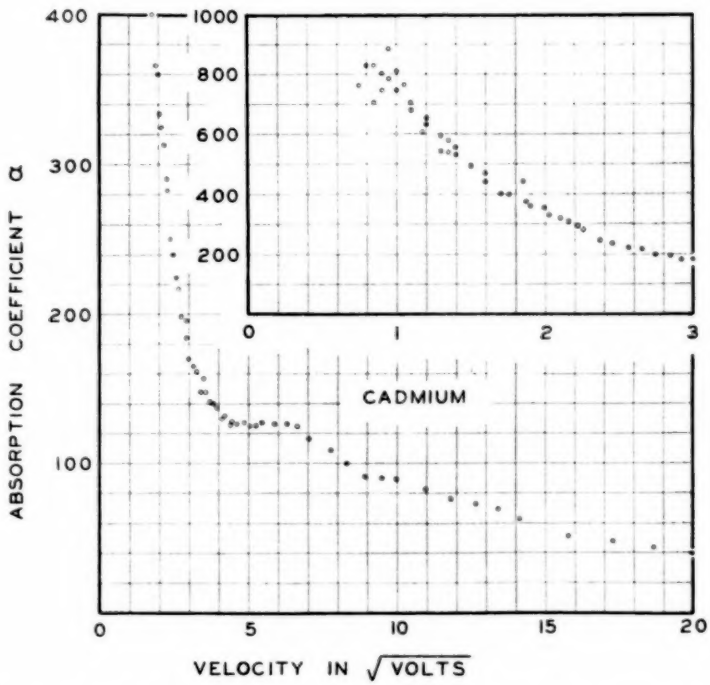

Fig. 2. The absorption coefficient α for electrons in cadmium vapor as a function of the velocity of the electrons.

reduced to 0°C and 1 mm of Hg pressure. The constants of the vapor pressure equation were taken from those given in the International Critical Tables.[8]

[8] International Critical Tables, Vol. III, p. 205.

These constants for zinc and cadmium are much more accurately determined than those for the alkali metals. The principle source of uncertainty in the values of the absorption coefficients is not due to the vapor pressure constants in this case but to the determination of the temperature. From the uncertainty in the temperature, not over 2°C, the resulting absorption coefficients might be in error by about 5 percent. Small differences in the temperature could be measured to 0.1°C.

Samples of the metals were used which were over 99 percent pure. These were distilled several times in vacuum and finally into the apparatus, which had previously been baked at 500°C for several hours, and the metal

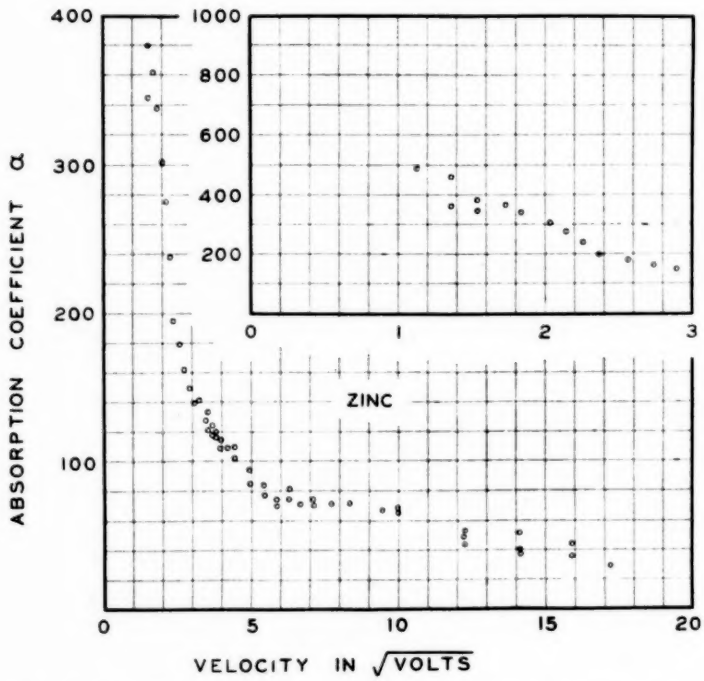

Fig. 3. The absorption coefficient α for electrons in zinc vapor as a function of the velocity of the electrons.

parts glowed by an induction furnace. This treatment was effective in removing the gases absorbed in the cadmium and zinc as measurements of the absorption coefficient were constant over a period of two months in a closed apparatus.

By plotting the log of the ratio of the current at the end of the path to the current from the slit in the cylinder, S_c, against the pressure, a straight line was obtained. The slope of the line gave the value of the absorption coefficient for unit pressure. Figs. 2 and 3 show the resulting values of the absorption coefficient for cadmium and zinc. Each point is the result of measurements at from 3 to 5 different pressures. Due to increasing leakage currents above 300°C, the data obtained with zinc were not as consistent as

those obtained with cadmium. The data taken with the two different experimental arrangements in cadmium are shown on the graph and are seen to be in excellent agreement. In the upper right portion of each graph the low velocity measurements are plotted. In cadmium the measurements were taken to 0.5 volts but, due to the leakage currents at the higher temperature used with zinc, the measurements could not be extended to 1.0 volt in zinc. There is an indication that the absorption coefficient in cadmium ceases to rise as rapidly below one volt as above one volt.

The opening of the final slit determines the maximum angle through which an electron may be deflected without being measured as absorbed. In

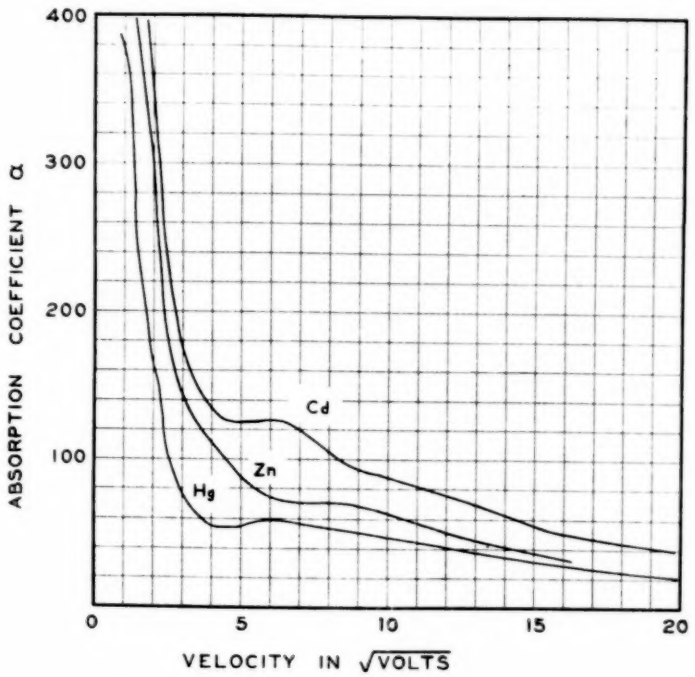

Fig. 4. The absorption coefficient α for electrons in cadmium, zinc and mercury vapors as a function of the velocities of the electrons.

cadmium two systems of slits and chambers were used with different limiting angles but the values of the absorption coefficient were not changed. Measurements by several observers on mercury[7] gave results that are quite consistent although the chambers used were geometrically quite different. This would indicate that the number of electrons scattered through small angles is only a small fraction of the total number of scattered electrons. These results are not in agreement with the measurements of Arnot[9] which indicate that a large fraction of the electrons of 82 volts velocity in mercury vapor are scattered in small angles. An apparatus with an adjustable aperture is being constructed to test this point.

[9] Arnot, Roy. Soc. Proc. **A125,** 660 (1929).

In Fig. 4 the curves for cadmium and zinc are compared with that for mercury. The values of α for mercury[7] have been changed from those due to vapor pressure data in Landolt and Börnstein's tables used in the original report to the data given in the International Critical Tables[10] from which the vapor pressure data for cadmium and zinc were also taken. This involves an increase of about 10 percent in the values of α. The character of all the three curves is the same; a very large effective cross-section for slow electrons which decreases rapidly with increasing velocity to a minimum, then rises slightly to a faint maximum followed by a steady decrease with further increase in velocity.

The curves indicate that cadmium is the largest of the three, zinc is next, and mercury is the smallest. This is the order of size to be expected rather than that of increasing atomic weight. The classical scattering of electrons due to the polarization of the atom by a passing electron was shown by Zwicky[11] to give the right order of magnitude for the absorption coefficients in the noble gases at velocities above the maximum in the curves. The absorption coefficient was proportional to the molar refractivity. The molar refractivities for these elements are Cd = 20.0 Zn = 14.6, and Hg = 13.7. This same agreement between the absorption coefficients and molar refractivity is found in the alkali vapors. The effective size of an atom is also indicated by its ionization potential. Helium, with the highest ionization potential, has one of the smallest effective cross-sections of any observed atom while caesium, with the lowest ionization potential, has the largest effective cross-section. The ionization potentials of the elements studied in this paper are Cd 8.9 volts, Zn 9.4 volts and Hg 10.4 volts. In the curves of elements not in the same row of the periodic table and therefore of different shape, it is not always easy to designate one as larger than the other. In general, however, it seems to be true that the magnitude of the absorption coefficient or the effective collision cross-section of an atom is proportional to the molar refractivity and inversely proportional to the ionization potential.

[10] International Critical Tables, Vol. III, p. 206.
[11] F. Zwicky, Phys. Zeits. **24**, 171 (1923).

COHESION IN MONOVALENT METALS

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(Received January 27, 1930)

Abstract

The theory of metallic structure, of Sommerfeld, Heisenberg, and Bloch, is carried far enough to explain cohesive forces, and calculations are made for atoms with one valence electron, particularly metallic sodium. The numerical results, though rough, are in qualitative agreement with experiment. It is found that the forces in general are of the same nature as those met in ordinary homopolar binding, discussed by Heitler and London; except that the purely electrostatic force from penetration of one atom by another is relatively more important, the valence effect from the exchange of electrons relatively less important, than in diatomic molecules.

As a preliminary to the calculation, the relations of the methods of Heisenberg and of Bloch are discussed, and it is shown that they are essentially equivalent in their results when properly handled. Remarks are made both about conductivity and ferromagnetism. In connection with conduction, it is shown that a definite meaning can be given to free electrons, that they are necessary to conduction, and that a method can be set up for computing their number, which is rather small compared with the number of atoms. Ferromagnetism is discussed in connection with a recent paper of Bloch. It is shown that a metal like an alkali cannot be ferromagnetic, for atoms at such a distance that the interatomic forces keep the metal in equilibrium, are too close to be magnetic. For ferromagnetism, rather, it seems necessary to have one group of electrons responsible for cohesion, and another group, of smaller orbit and therefore relatively farther apart, producing the magnetism; a situation actually found only in the iron group and the similar groups.

I. Introduction

A CRYSTAL of a metal is an enormous molecule, with electronic energy levels depending on the positions of all the nuclei, just as the electronic energy of a diatomic molecule depends on the internuclear distance. In this paper, in which we are interested in cohesive forces, we must find this energy of the lowest state in terms of the size of the crystal. We limit ourselves to geometrically similar arrangements of the nuclei, with changing scale. From the minimum of the curve, we find the heat of dissociation, grating space, and compressibility of the metal. But also we can investigate the wave function of this lowest state, and obtain information about the electric and magnetic properties of the metal. In this way we are naturally led to a discussion of the calculations of Heisenberg[1] and of Bloch on these subjects; in order to be sure that we really understand the arrangement of energy levels, we discuss the relationships of their methods, and arrive at a consistent picture combining them.

[1] W. Heisenberg, Zeits. f. Physik **49**, 619 (1928); F. Bloch, *ibid.* **52**, 555 (1929).

As for the results, one naturally asks first, what are the forces holding a metal together? Are they ordinary attractions on account of penetration of atoms, or valence forces, or electrostatic forces of ionic attraction, or van der Waals forces, or some special sort not found in other cases? This question cannot be answered categorically; no doubt all the forces are simultaneously present, and the problem is to find the relative magnitudes. The tentative result at which we arrive is that the simple penetration of one atom by another is the most important part of the effect. But valence effects are also present, although weakened by having the valences shared by many neighbors, and are responsible for a considerable fraction of the attraction. Although these actual magnitudes may not be verified by more accurate calculation, still we have discussed the problem in enough detail so that the general relations can be understood in any case.

The other question one will ask is, what is the situation of the electrons in the metal? Can one give a meaning to the question, how many free electrons are there? The answer, from whichever side we look at the question, seems to be the same. Most of the valence electrons are at any time attached to their atoms. These electrons cannot take part in conduction; they could do it only by having a whole file of such electrons simultaneously jump to the next atom in line, a most unlikely occurrence. But a few electrons at any time—calculation suggests a few percent—will be detached from their atoms, leaving an equal number of positive ions behind them; and they are what, by all rights, one should call free electrons. These electrons, and the positive ions left behind, can take part in conduction. First, the free electrons can move easily from one atom to the next. Second, a bound or associated electron on one of the atoms next a positive ion can jump to that ion, leaving its own atom ionized. We are thus led precisely to the dual theory of conduction, by free and by associated electrons, which Professor Hall[2] has suggested and elaborated. When we look at the metal by the method of Heisenberg, these results become clear. In that method, a wave function consists of the assignment of electrons to atoms. We find that we must go beyond Heisenberg, in assigning sometimes two electrons to one atom, sometimes none, instead of always one; for we need such states to solve the problem of the stationary states of the metal. That is, we introduce free electrons. And when we consider transitions from one state to another, it is easy to see that these transitions can result in conduction only when such free electrons are present. On Bloch's scheme, where we describe directly the velocity, rather than the position, of the electrons, it is less easy to see the relation; but here too one can show that, if there are no free electrons, the velocities of all electrons must compensate, so that there is no net current. Since this paper is not primarily about conduction, we do not go into these points with any detail.

The only metals specifically treated are those with one valence electron per atom, and that in an *s* state; that is, the alkalies. And it is assumed that they can be replaced by single valence electrons moving in non-coulomb

[2] E. H. Hall, Proc. Nat. Acad., 1920–1921.

fields. This can be easily justified. It is to be noted that the other metals are more complicated, not merely by having more electrons, but by having them in p or d orbits, thus introducing new degeneracies. The actual calculations of cohesion have been carried through for sodium, with satisfactory results. They are only done roughly, however; the primary purpose of this paper is to make clear the general relations, rather than to attempt accurate calculations. The work is being carried further by Dr. Bartlett, and I wish to thank him for help on some of the calculations used in this paper. The work described here has been done while the writer was on leave, working in Leipzig. He wishes to thank Professor Heisenberg for his courtesy in extending the privileges of his laboratory, and for a number of illuminating conversations on the subject of the paper; and also to thank Harvard University for granting leave, and the Guggenheim Foundation for the assistance of a fellowship.

2. Comparison of Heisenberg's and Bloch's Methods

The problem of a metal must be attacked by perturbation theory, and the unperturbed functions which we use can be set up in two quite different ways, one used by Heisenberg, the other by Bloch, either giving us a finite set of unperturbed functions. We regard the perturbation problem in the following way: we seek those linear combinations of these functions which, in the sense of the variation method, form the best approximations to solutions of Schrödinger's equation. This problem is solved by computing the matrix of the energy operator with respect to these functions, and solving the equations

$$\sum_k (H(i/k) - \delta(i/k)W)S(k) = 0$$

for the coefficients $S(k)$ to be used in making the linear combinations, and the energy values W of the resulting terms. (The term $\delta\ (i/k)$ must be given a slightly different form if the unperturbed functions are not orthogonal). This differs from the more conventional method: there one starts with an infinite, complete set of unperturbed functions, instead of our finite set, but solves only as a power series in the non-diagonal terms of the energy matrix, breaking off after the second power in all ordinary applications. It resembles more closely the quite different method ordinarily used with degenerate systems, where one takes only very few unperturbed states, but correctly solves the problem of combining them. For a nearly degenerate problem like the present one, with a great many states near together, the conventional method of developing in series will not work well, for the series do not converge well, and we are forced to use something like the present method. The justification comes simply from the assumption that the lowest states can be well approximated by such a linear combination of Heisenberg's or Bloch's functions (which correspond to having the atoms in their normal states). Surely this is not exact; for better results we should have to consider also the excited states of the atoms. But also certainly it is a fair approximation for the lowest states of the metal.

Heisenberg's functions, amplified in a simple way, form good approximations when the crystal is extended, for they are derived from the separated atoms. Bloch's functions on the other hand come by analogy with the free electron theory of Sommerfeld, and are good approximations when the crystal is compressed. The actual solutions of the perturbation problem are of course linear combinations of either Heisenberg's or Bloch's functions, not individual ones, and one gets the same final result whichever set one starts with (for the two sets of functions can be written as linear combinations of each other). But the fact that in the limiting cases the functions of one of the two sets become rather good approximations can be used, along with interpolation, to derive the general nature of the real stationary states. This comparison is made in the present section, and is illustrated by the interesting case of H_2, where the calculations can be made exactly. At the outset, we must recognize two facts: first, that we must amplify Heisenberg's method by including polar states, to make it general enough to agree with Bloch's and to permit conductivity; second, that although Bloch has the proper set of functions, he has nowhere attempted to solve the perturbation problem, but has merely taken his unperturbed functions as being correct, which amounts to getting the energy to the accuracy of the conventional "first order perturbations."

The first step in either Heisenberg's or Bloch's method, as we apply them, is to write an approximate solution as a product of functions of the individual electrons. Heisenberg takes, for these separate functions, the wave functions of electrons attached to individual nuclei; the number of such functions is the product of the number of nuclei, multiplied by the number of different sets of quantum numbers we consider for an individual nucleus. If we restrict ourselves to s states, there are then only two states per nucleus, corresponding to the two orientations of the spin. For nucleus a, we denote these two[3] by $u_\alpha(a/x)$, $u_\beta(a/x)$, and we have such a function for each nucleus $a\ b\ \ldots\ n$. Bloch takes, on the other hand, combinations of these functions:

$$u_\alpha(klm/xyz) = \sum_{g_1 g_2 g_3} e^{2\pi i(kg_1/G_1 + lg_2/G_2 + mg_3/G_3)} u_\alpha(g_1 g_2 g_3/xyz),$$

where $g_1g_2g_3$ are the coordinates of a particular nucleus, $G_1G_2G_3$ the dimensions of the rectangular crystal, and $u_\alpha(g_1g_2g_3/xyz)$ the wave function (as used by Heisenberg) for an electron moving around the nucleus situated at $g_1g_2g_3$. The function with k, l, m represents an electron, in general moving in the direction k, l, m, but pausing at the various atoms on the way. There are as many sets k, l, m allowed as there are atoms in the crystal; for larger k, l, m the function proves to be merely a repetition of one already counted.

[3] We use here for convenience in writing Pauli's notation u_α, u_β for the spin, rather than the more explicit but more cumbersome notation $u(n/x_i)\ \delta(m_s/m_{si})$ used in a previous paper. See J. C. Slater, Phys. Rev. **34**, 1293 (1929). The method used in the present paper is described, as applied to atoms, in the paper referred to; it should be understood that, although we speak here of using Heisenberg's and Bloch's methods, our actual procedure is quite different from that of these authors.

Now we actually set up the product of functions mentioned in the previous paragraph: we pick one out and let it be a function of the coordinates x_1 of the first electron, a second for the coordinates x_2 of the second, and so on to the nth, and multiply them all together. By the exclusion principle, no function can be chosen more than once. Then we form an antisymmetric combination, by permuting the indices of the electron coordinates, and adding the permuted functions with appropriate signs, obtaining essentially a determinant. These antisymmetric functions are the ones with which we start our perturbation calculation. Many such functions can be set up: there are $2n$ functions of a single electron, of which only n are to be chosen for each antisymmetric function, so that there are $(2n)!/(n!)^2$ different functions. Our perturbation problem is that of finding which linear combinations of these functions most nearly satisfy the wave equation. We may note the restriction of Heisenberg's method as he uses it; he does not include polar states. That is, he does not allow for example the two functions $u_\alpha(a/x)$, $u_\beta(a/x)$ to appear together in any product. This greatly limits the number of functions; but although the terms obtained by it certainly represent the lowest energy levels, since it requires energy to form a positive and a negative ion from two neutral atoms, we do not make this limitation.

Having set up the unperturbed functions, we next make linear combinations of them, by the method described in a previous paragraph. This process can be simplified by using a property of the spin. Every unperturbed function has a certain definite component M_S of spin along the axis, equal to $(n_\alpha - n_\beta)/2$, where n_α is the number of electrons with positive component of spin, n_β the number with negative. If now we neglect the magnetic interaction between the spins and the orbital motion, the problems with each value of M_S can be handled separately: the components $H(i/j)$ from a function with one value to a function with another are zero. The states with a given M_S include, as one readily sees, all those states whose total spin S is equal to or greater than M_S (for just these S's can be so oriented, on the vector model, as to give a component M_S along a fixed axis). Thus by solving each such problem, and comparing, we can identify the spin of each term.[4]

The two methods can be illustrated by the case of H_2. Here there are $4!/(2!)^2=6$ different wave functions. On Heisenberg's method, the four functions for an individual electron can be symbolized by (αa), (βa), (αb), (βb); two of these are to be picked out for each antisymmetric wave function. Thus the six are $(\alpha a)(\alpha b)$; $(\alpha a)(\beta a)$, $(\alpha b)(\beta b)$; $(\alpha a)(\beta b)$, $(\beta a)(\alpha b)$; $(\beta a)(\beta b)$. They are arranged, first, by M_S: the first has the value 1, the next four the value 0, and the last -1. Thus the terms consist of one triplet and three singlets. Among the four terms with $M_S=0$, the first two are polar (and not considered by Heitler and London, or Heisenberg), the last two are non-polar. Immediately one finds that the sum of these non-polar functions is the component of the triplet. We are then left with three functions: the

[4] This is essentially the method used in the paper already quoted It has already been applied by Bloch to problems in the theory of metals. See F. Bloch, Zeits. f. Physik., **57**, 545 (1929).

two polar ones, and the difference of the non-polar ones, from which to find our three singlets. The difference of the polar ones is antisymmetric in the nuclei, giving one state; their sum, and the difference of the non-polar functions, give two functions symmetrical in the nuclei, between which we finally solve the simple perturbation, resulting now in a quadratic secular equation, and obtain the two remaining singlet states. The energy levels as a function of the distance of separation are plotted in Fig. 1. The energy level of the lowest, $^1\Sigma S^N$, is almost exactly as given by Heitler and London, but its wave function contains quite an appreciable contribution from the polar state. The triplet is just the repulsive state of Heitler and London. The other two levels are essentially polar. They go at infinite separation to the energy of $H^+ + H^-$, greater than the other limit by the ionization potential less the electron affinity of H (this rough approximation gives $-\frac{1}{4}Rh$ for the electron

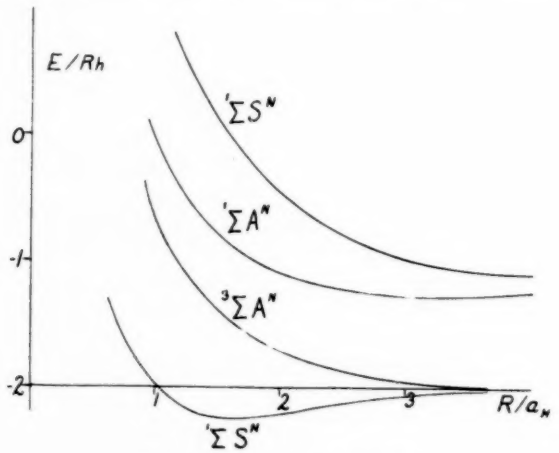

Fig. 1. Energy levels of H_2.

affinity, so that the terms go to $5/4Rh$). The lower of these has a minimum; it is presumably the polar part which, by combination with other functions, leads to the experimentally known B state of the molecule. We notice that at large separations the functions behave just like Heisenberg's (extended) unperturbed functions: a triplet and a singlet are non-polar, and go to the lower energy; while two singlets are polar, and go to the higher level.

Next we consider Bloch's method for the same problem. His functions for one electron, for this case, are

$$u_\alpha(0/x) = u_\alpha(a/x) + u_\alpha(b/x)$$
$$u_\alpha(1/x) = u_\alpha(a/x) - u_\alpha(b/x),$$

with similar functions for β. (These do not follow quite directly from the general formulas given above; Bloch's functions must be slightly modified for finite systems, for they apply rather to infinite but periodic ones.) The discussion of multiplicity given above goes through without change, if we only substitute 0, 1 for a, b. We can easily show by direct calculation

that the resulting unperturbed antisymmetric functions are linear combinations of those found by Heisenberg's method. For example, for $M_S=1$, there is only one function by either method, so these must be identical, except for a numerical factor. By Heisenberg's method the function is

$$u_a(a/x_1)u_a(b/x_2)-u_a(b/x_1)u_a(a/x_2).$$

By Bloch's it is

$$\begin{aligned}
&u_a(0/x_1)u_a(1/x_2)-u_a(1/x_1)u_a(0/x_2)\\
&\quad=[u_a(a/x_1)+u_a(b/x_1)][u_a(a/x_2)-u_a(b/x_2)]\\
&\qquad-[u_a(a/x_1)-u_a(b/x_1)][u_a(a/x_2)+u_a(b/x_2)]\\
&\quad=-2[u_a(a/x_1)u_a(b/x_2)-u_a(b/x_1)u_a(a/x_2)].
\end{aligned}$$

We can set up the whole perturbation problem in these functions; and the solution can be carried out as easily as before, leading of course to just the same answers. The interesting question now is, how closely do Bloch's individual functions approximate the correct ones, for small values of R? The functions are respectively as follows: a singlet with both electrons in the state 0; a singlet and triplet with one in the state 0, the other in the state 1; and a singlet with both in the state 1. The state 0 corresponds to the lowest vibrational state on Sommerfeld's theory, the state 1 to the next higher one, so that the first state has on the simple interpretation only the zero-point vibrational energy, the next two have each one quantum, and the last two. Examination of the actual wave functions shows that they agree quite closely with the functions of Bloch: the lowest one is made, it is true, by combination of the (00) and (11) states, both being S^N, but the coefficient of the first is about eight times as large as that of the second, when R is such that the energy is at its minimum. The next two are made up of the (01) states. The highest is about eight parts of (11) to one of (00). The energies also show, for high compression, the behavior expected: the two states which should have one quantum of vibrational energy draw together, and the one with two quanta is just about twice as far above the lowest state as those with one. Even the spacing of these levels is just about what would be calculated on Sommerfeld's theory for an electron vibrating in a region the size of the molecule. Thus we see that Bloch's unperturbed functions form fairly good approximations to the real functions for the compressed state, as Heisenberg's do for the extended state.

We can now return to the general case, and make use of the fact that Heisenberg's functions approximate the real wave functions well for large separations, Bloch's for small. First, for the extended system, the energy is the ionization energy, on account of having many ions as well as neutral atoms. For a metal, it requires about 6 volts to form a positive and negative ion from two neutral atoms. Thus if all the atoms were ionized, we should have $n/2$ such pairs, or an energy per atom, or per electron, of about 3 volts. This measures the extension of the group of terms, for large R. It is a simple problem in permutations to find the number of terms of each multiplicity

with each energy value in the limit. The one term of highest multiplicity will approach the lowest limit, for large R; it must be entirely nonpolar, for all spins point in the same direction, so that no two electrons can be in the same atom. For the next lower multiplicity, only one electron has a reversed spin; it is the only one which can be in an atom with another electron, so that there can be just one pair of atoms ionized. Following out, we easily see that terms of lower and lower multiplicity, in the limit of large R, lie higher and higher, and at the same time are more and more spread out. They spread in such a way that there are terms of each multiplicity way down to the bottom limit, although not to the top. As we shall see later, for R large but not infinite, in the normal case, the really lowest terms have small spins; but near them are many terms with large spin.

For the compressed system, the arrangement is as given by Bloch's theory. The total extension of the group of terms increases with $1/R^2$; for ordinary values of R, it is of the order of the mean zero-point energy, times n, which is decidedly larger than 3 volts$\times n$. Thus not only do the curves tend upward for decreasing R, giving repulsive energy levels, but they are definitely doing this at the actual size of the metal. The general physical interpretation of this repulsion is obvious: the valence electrons act here approximately as a perfect gas, and the energy levels are those of such a gas as it is compressed adiabatically against gas pressure, the energy varying therefore as $V^{-2/3}$ or as $1/R^2$. Here the terms of high multiplicity lie in the center of the pattern; those of lower spin also average in the center, but are more and more spread out. Since the terms of high spin are so low for large R, but not for small R, they must be even more repulsive than the others. The possibility seems very remote that any terms except those with very low multiplicity could be so low as to have minima, and come into the question for the normal state. We see that for cohesion we are interested only in the very lowest fraction of the whole set of terms. These terms almost all will go to the lowest energy level at infinite separation; they become in this limit non-polar. And the accuracy with which one can compute the lowest states of H_2 from Heitler and London's non-polar functions suggests that here too this may be possible. Accordingly for our actual calculation of these lowest states, we shall use Heisenberg's method with only non-polar functions. We shall find here, as we expect from our qualitative discussion, that the terms of low multiplicity really do lie below, some of them being attractive; while those of high multiplicity are repulsive, the highest spins lying highest. Finally we shall consider the effect of polar terms, and conclude that it is really small on the low energy levels, although not on the wave functions; for it is the polar character of the wave functions which makes conductivity possible.

3. Electric and Magnetic Properties

Conductivity. In the introduction we have mentioned the interpretation of electric conduction on Heisenberg's and on Bloch's scheme. One notices that a single one of Bloch's functions implies conduction—the diagonal term

of the momentum matrix is different from zero—whereas with Heisenberg's functions we must have a continual change from one stationary state to another. But it is particularly important to notice that, without polar states, or free electrons, no conduction is possible; we cannot set up combinations of non-polar states with a resultant momentum. For example, with two electrons, we can set up an arbitrary non-polar function $c_1u(a/x_1)u(b/x_2)+c_2u(b/x_1)u(a/x_2)$. If now we compute the momentum, whose operator is $h/2\pi i(\partial/\partial x_1+\partial/\partial x_2)$, the only possibly significant terms are the cross terms, like

$$c_1c_2\frac{h}{2\pi i}\int u(a/x_1)u(b/x_2)\left(\frac{\partial}{\partial x_1}+\frac{\partial}{\partial x_2}\right)u(b/x_1)u(a/x_2)dv_1dv_2$$

$$=c_1c_2\frac{h}{2\pi i}\left\{\int u(b/x_2)u(a/x_2)dv_2\int u(a/x_1)\frac{\partial}{\partial x_1}u(b/x_1)dv_1\right.$$

$$\left.+\int u(a/x_1)u(b/x_1)dv_1\int u(b/x_2)\frac{\partial}{\partial x_2}u(a/x_2)dv_2\right\}.$$

On account of the penetration of one atom by the other, the integrals $\int u(b/x_2)u(a/x_2)dv_2$ are not zero. The integral $\int u(a/x_1)(\partial/\partial x_1)u(b/x_1)dv_1$ is also different from zero. But it is exactly cancelled by $\int u(b/x_2)(\partial/\partial x_2)u(a/x_2)dv_2$, as one can show by Green's theorem, so that the whole is zero. On the other hand, if we set up a polar combination like $c_1u(a/x_1)u(a/x_2)+c_2u(b/x_1)u(b/x_2)$, we again get two terms, but now they add, and give a current. As another example, we can take the term of maximum multiplicity in any system. In this term, we have seen by Heisenberg's scheme that each atom has just one electron, so that we expect no conduction. But in Bloch's scheme, each value k, l, m has just one electron. Since each such value is balanced by one with $-k, -l, -m$, having opposite momentum, the total momentum is zero, and there is again no current.

We can now see the importance of considering exactly the wave functions, as well as the energy levels, of the lowest state. In the ordinary low states there will, of course, be no current. But near the lowest state, if there is to be conductivity, there must be combinations of polar states, having a current, which are assumed in the presence of a field, and whose added energy comes simply from the kinetic energy of the electrons and the self-induction. Such states are possible only on account of the presence of positive and negative ions, with the resulting free and associated electron conductivity.

Magnetism. The lowest state of H_2 is the non-magnetic $^1\Sigma$, and we have found such a situation in general. In the region where the lowest states have their minimum, the metal must surely be in a compressed state, Bloch's arrangement of energy levels must be a good approximation, and the states of large spin must lie very high. We are thus led to the quite general conclusion that the outer electrons, which are largely if not entirely responsible for both cohesion and conduction, cannot produce ferromagnetic effects. If a metal is to be ferromagnetic, there must then be other electrons than these

outer ones which are responsible for it, and these others must have smaller orbits, so that at the equilibrium distance of the outermost ones, the inner ones will be relatively further apart, and can be treated as an extended rather than as a compressed system. It is a very attractive hypothesis to suppose that in the iron group the existence of the $3d$ and $4s$ electrons provides in this way the two electron groups apparently necessary for ferromagnetism; for it is only in the transition groups that we have two such sets of electrons, and this criterion would go far toward limiting ferromagnetism to the metals actually showing it.

We next ask just how such inner electrons could be ferromagnetic. Certainly the general trend of the terms of high spin to the low energy values at large R is an essential part of the question: there will be terms of large spin near the lowest level. Bloch[5] has discussed the problem, concluding that for large R's the terms of high spin actually lie lower than those of smaller spin (he does not specifically discuss the dependence on R, but his energy formulas all contain it parametrically). This conclusion, however, is not correct; Bloch has merely computed diagonal values of the energy, with respect to his functions, and for large R these by no means form approximations to the actual energy values. From the correct treatment of the problem as we have given it, it is plain that at all R's there are terms of low multiplicity as low as those of high spin, or lower. It may be, however, that the mere presence of so many low terms of high multiplicity may be enough, on account of their high *a priori* probability and large number, to insure that the terms of large spin should be well represented at ordinary temperatures, even though there are low terms of zero spin, and so produce ferromagnetism. If, however, this should prove on calculation not to give the right effect, we should be led to consider Heisenberg's assumption that the normal order of terms is inverted in ferromagnetic atoms, the terms of high multiplicity lying lowest. He has shown by a general argument that electrons of large total quantum number (which the $4s$ electrons of iron have) have an exchange integral of the opposite sign to that found in hydrogen, so that the order of the non-polar terms would be reversed. This we should fit into our scheme in the following way: although this exchange integral is anomalous at large R, it presumably changes sign and becomes normal at smaller R; for first, Heisenberg's general argument only applies at large R; and second, our condition that the energy levels should approach those of Bloch at small R, with the terms of large spin lying high, seems quite general. Thus we should assume that the terms at small R lie as in Fig .1 but that at a considerable value of R, there is a crossing over (in this case the ${}^3\Sigma A^N$ crossing and lying under the ${}^1\Sigma S^N$), described by a change in the sign of the exchange integral K used in the next section from negative to positive. By assuming the existence of an inner group of electrons with these properties, we seem to secure a consistent picture of ferromagnetism. On the other hand, of course it is always possible that ferromagnetism is connected with the fact that the valence electrons of iron have an orbital angular momentum different from zero.

[5] F. Bloch, Zeits. f. Physik, **57**, 545 (1929).

4. Cohesion

We are now prepared to begin the actual calculation of the lowest stationary states. We make several simplifications, which we later remove. First, we consider only non-polar states, in Heisenberg's scheme, and disregard exchange integrals except between adjacent atoms; this is the approximation also made by Heisenberg. Finally, for the present, we consider a linear lattice, n atoms uniformly spaced along a line, rather than a space lattice. Our problem, of course, is to compute the matrix of the energy with respect to the wave functions we have chosen, and then solve the problem of making proper linear combinations. The computation of the matrix is simple. By a fundamental formula of the previous paper mentioned above, the diagonal components are a sum, first, of the energies of the separate atoms, which we need not consider; next, a sum over all adjacent pairs, as the pair of atoms a and b, of integrals $J(a/b)$, which is essentially the diagonal energy E_1 of Heitler and London; finally, a sum over all adjacent pairs which have the same spin, of terms $-K(a/b)$, where K is the exchange integral E_2 of Heitler and London. Further, it is easy to show that all non-diagonal terms are zero, except those for which the distributions in the two states differ only by the exchange of an adjacent α and β; in such cases, the term is $-K$. In the normal case, to which we shall refer specifically, J and K as functions of R are both negative, K numerically greater than J. But in Heisenberg's case, K must be taken to be positive for large R, although presumably negative for small R.

To illustrate by H_2, we have one state with both spins parallel; then the energy is $J-K$. Next we have the problems with one parallel, the other anti-parallel; there are two such states (the two polar ones being omitted). Each has the diagonal energy J, and the non-diagonal energy between them is $-K$. Thus the equations for the linear combinations are

$$(J-W)S(1)-KS(2)=0$$
$$-KS(1)+(J-W)S(2)=0,$$

giving energy values $W=J\pm K$, the first evidently being the singlet, the second the component of the triplet.

In the general case, the computation of the matrix is no more difficult; the real problem is the solution of the linear equations for the S's. We cannot do this exactly; but we adopt two methods of approximation, one holding for larger spins, the other for smaller spins. We first discuss the former.

Method for large spins. First we take the problem where all spins are parallel, $n_\alpha=n$, $n_\beta=0$. Here there is but one state. Since with our linear lattice there are $(n-1)$ adjacent pairs, and all spins are parallel, the energy is simply $(n-1)J-(n-1)K$. Since J and K are normally both negative, but K numerically greater than J, this is a positive energy for all values of R, and results in a repulsive term. For Heisenberg's case, on the other hand, K is positive, and this term is attractive. Next we take the problem $n_\alpha=n-1$, $n_\beta=1$. There are now n unperturbed wave functions: the one electron β can

be attached to any of the n atoms. We number the functions by the number of the atom where the electron is, only decreased by $\frac{1}{2}$: we have $u_{1/2} \cdots u_{n-1/2}$. Each of these functions will have the diagonal energy $(n-1)J-(n-3)K$, since two of the adjacent pairs now have opposite spins, except for the two functions $u_{1/2}$ and $u_{n-1/2}$ where our β electron is at an end of the lattice, and the energy is $(n-1)J-(n-2)K$. Also, all non-diagonal terms will be zero except those between terms of adjacent number, as for example between those symbolized by

$$\cdots \alpha\,\alpha\,\alpha\,\beta\,\alpha\,\alpha\,\alpha \cdots$$

and

$$\cdots \alpha\,\alpha\,\alpha\,\alpha\,\beta\,\alpha\,\alpha \cdots,$$

and which differ by just one interchange of an α and β. As a result, the perturbation equations will be

$$[(n-1)J-(n-2)K-W]S\left(\frac{1}{2}\right)-KS\left(\frac{3}{2}\right)=0$$

$$-KS\left(\frac{1}{2}\right)+[(n-1)J-(n-3)K-W]S\left(\frac{3}{2}\right)-KS\left(\frac{5}{2}\right)=0$$

$$-KS\left(\frac{3}{2}\right)+[(n-1)J-(n-3)K-W]S\left(\frac{5}{2}\right)-KS\left(\frac{7}{2}\right)=0$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$-KS\left(n-\frac{3}{2}\right)+[(n-1)J-(n-2)K-W]S\left(n-\frac{1}{2}\right)=0$$

These equations are easily solved; they occur, for example, in the problem of a string weighted at equal intervals,[6] the S's being the displacements of the weights. To solve, we merely assume $S(k)=\frac{\cos}{\sin}(\alpha k)$. The first and last equations give boundary conditions. They become like the others if we introduce an $S(-\frac{1}{2})$ and $S(n+\frac{1}{2})$, the first equation becoming

$$-KS(-\tfrac{1}{2})+[(n-1)J-(n-3)K-W]S(\tfrac{1}{2})-KS(\tfrac{3}{2})=0,$$

and if we further set $S(-\frac{1}{2})=S(\frac{1}{2})$ and $S(n+\frac{1}{2})=S(n-\frac{1}{2})$. These are then the boundary conditions; and to satisfy them we must take

$$S(k/p)=\cos p\pi k/n, \quad \text{where} \quad p=0,1,\cdots,n-1.$$

Now we substitute this form in our difference equations; and we get for W

$$-K\left(\cos\frac{p\pi}{n}(k-1)+\cos\frac{p\pi}{n}(k+1)\right)+[(n-1)J-(n-3)K-W(p)]\cos\frac{p\pi k}{n}=0,$$

from which in each case

$$W(p)=(n-1)J-(n-3)K-2K\cos\frac{p\pi}{n}.$$

[6] See, for example, Rayleigh's "Theory of Sound."

We now have the transformation coefficients $S(k/p)$ and the energy values $W(p)$ for the rotation of axes to the pth stationary state; the W's are the exact energy levels. They are evidently distributed between the values $W(0)=(n-1)J-(n-1)K$, and $W(n-1)=(n-1)J-(n-3-2\cos\pi(n-1)/n)K=(n-1)J-(n-5)K$, almost, for large n. Obviously $W(0)$ is the energy of the level of highest multiplicity, which we have found before. Thus the levels $1\cdots(n-1)$ are those of next to highest multiplicity.

Next we take the problem with two electrons of spin β. There are $n(n-1)/2$ such terms: each of the two indistinguishable β's can be on any one of the n atoms, so long as they are not on the same atom. Now it is convenient to denote states by the two atoms, say i and j (each going from $\frac{1}{2}$ to $n-\frac{1}{2}$) on which electrons β are. Our problem becomes analogous to that of a square membrane loaded at equally spaced points. The diagonal terms of the energy are all $(n-1)J-(n-5)K$, unless one of the β's is at an end of the lattice, or unless the two β's are adjacent. There are four non-diagonal terms for transitions from each wave function: for $i\rightarrow i\pm1$, or for $j\rightarrow j\pm1$. A typical equation can be written

$$\begin{aligned}&-KS(i,j-1)\\ -KS(i-1,j)&+[(n-1)J-(n-5)K-W]S(ij)-KS(i+1,j)\\ &-KS(i,j+1)=0.\end{aligned}$$

This we satisfy by a product of cosine functions, $S(ij/pq)=\cos(p\pi i/n)\cos(q\pi j/n)$. We easily find that these exactly satisfy the boundary conditions when i or $j=\frac{1}{2}$ or $n-\frac{1}{2}$. There remains the condition when i is nearly equal to j. If $i=j\pm1$, the diagonal energy is $(n-1)J-(n-3)K$, since the two β's are together; on the other hand, since the β's cannot be on the same atom, the coefficients $S(jj)$ and $S(j+1,\ j+1)$ vanish, so that only two transitions, rather than four, are possible. If now we define an $S(jj)$ and $S(j+1,j+1)$, we can make the equations of the same form as the general one, if only $S(jj)+S(j+1,\ j+1)=2S(j+1,\ j)$. This furnishes our second boundary condition, which is evidently along the diagonal of our square "membrane." Unfortunately we cannot satisfy this condition exactly with our cosine functions; closer investigation shows that one must have much more complicated functions, with hyperbolic cosines, to satisfy it exactly, and one cannot carry the method through for the general case. Approximately, however, we can easily take care of our condition. If the p and q are not too great, so that the "wave-length" of the waves in our membrane is large, we can replace our condition by a differential one: it states that the amplitude at a point next the diagonal is the mean of the two adjacent values on the diagonal, and this very nearly means that the normal derivative of the function, at right angles to the diagonal, is zero. This we can satisfy by making our function symmetrical about the diagonal, or using $\cos(p\pi i/n)\cos(q\pi j/n)+\cos(q\pi i/n)\cos(p\pi j/n)$. We may expect this to hold best for small p and q, not so well for large values. It is clearly not right; for example, it yields $n^2/2$ functions, instead of the correct number $n(n-1)/2$.

Our function is an exact solution of the difference equations, if not of the boundary condition; and we find for the energy

$$W(p,q)=(n-1)J-(n-5)K-2K\left(\cos\frac{p\pi}{n}+\cos\frac{q\pi}{n}\right),$$

where p, q go from 0 to $n-1$, but each pair is counted only once. The term of highest multiplicity comes from $p=q=0$; the $(n-1)$ terms of next highest value are those with either p or $q=0$, but the other not; the remaining terms are of multiplicity smaller by two.

This result can now be generalized without trouble: if we have many β's, the energy levels are given by

$$W=(n-1)J-(n-1-2n_\beta)K-2K\sum_{i=1}^{n_\beta}\cos\frac{p_i\pi}{n},\quad p_i=0\cdots n-1.$$

The terms where one or more p_i's equal zero are those whose total spin is greater than $(n_\alpha-n_\beta)/2$; those with all p's different from zero are those whose total spin equals $(n_\alpha-n_\beta)/2$. The latter value is evidently enormously greater than the other: every spin has enormously more terms than any higher spin. Thus the terms of a given component of spin along the axis, and those of the same total spin, are approximately the same. We can at once find the distribution in energy of the terms of a given spin. They evidently cluster about the value $(n-1)J-(n-1-2n_\beta)K$; they are distributed about this value like the displacements of a point simultaneously acted on by a sum of n_β periodic vibrations of equal amplitudes but arbitrary phases. This gives, of course, approximately a Gauss distribution. The width of the distribution curve can be derived very easily: we compute the mean square deviation of the energy from its mean, $\overline{(W-\overline{W})^2}=4K^2\overline{[\Sigma\cos(p_i\pi/n)]^2}$, the average being taken when each p varies independently from 0 to n. We can take this variation to be continuous rather than discrete. Then the product terms in the square of the sum of cosines all average to zero, the square terms average to $\frac{1}{2}$, and the result is $2K^2n_\beta$. These results may be compared with those obtained by Heisenberg on the group theory, and which as Bloch has shown can also be found from the present method. In the notation of the present paper, putting the number of neighbors of each atom equal to 2, and leaving out the terms in J, Heisenberg finds

$$\overline{W}=-(n-2n_\beta+2n_\beta^2/n)K$$
$$\overline{(W-\overline{W})^2}=2K^2n_\beta(1-n_\beta/n)(1+2n_\beta/n-2(n_\beta/n)^2).$$

Our formulas agree with these exact ones to terms in n_β but no further, as we expect from the fact that our approximations hold only for small n_β. For small p's, as we have seen, our results should be good even for large n_β; for the case of ferromagnetism, when on Heisenberg's hypothesis the terms are reversed, these are the lowest terms, so that this result should be very useful here. In the normal case, however, the lowest terms are those of large p, and these are the ones we need for cohesion. About these lowest terms, we

can be fairly sure that they lie higher than the lowest ones we have found, or $(n-1)J-(n-1-4n_\beta)K$, since the mean lies higher than the mean we found. For zero spin, for example, we can be fairly sure that the term lies above $(n-1)J+nK$. But this value need not be a very good approximation; we actually find, by the method of the next section, that the lowest term for zero spin is about $(n-1)J+0.290nK$. Fortunately even this has a positive coefficient for K, and is so an attractive rather than a repulsive term.

Method for zero spin. For zero spin, $n_\alpha=n_\beta=n/2$, and there are $n!/(n/2!)^2$ terms. We adopt quite a different method of classifying them. Before, most of the terms of a given n_β had nearly the same diagonal energy; but now the range of energy is large, from $(n-1)J$ for the state with alternating α's and β's so that there are no parallel spins, to $(n-1)J-(n-2)K$ for the state where all the α's come at one end of the lattice, all the β's at the other. With this large range, we find it convenient to classify terms by their diagonal energies; and we find as we should expect, that for the lowest states of the perturbed system we must consider most the low unperturbed states. We do not need to take into account all states: we find that approximately (though by no means exactly) the terms can be divided into a number of non-combining sets, and we set up one such set in the following way. We commence with the lowest state, of energy $(n-1)J$, where α's and β's alternate. Next we consider the $n-1$ states which combine with it, coming from interchanging one pair, and each having the energy $(n-1)J-2K$, except those from the two end pairs, with energy $(n-1)J-K$. We leave these two out, retaining for our set the $n-3$ states which have the energy $(n-1)J-2K$. Each of these has $n-3$ states with which it combines, coming from interchange of one of the $n-3$ adjacent pairs with opposite spins. Of these $n-3$, the two in which the new interchanged pair is next the one already interchanged have the energy $(n-1)J-2K$; the one in which the pair already interchanged is changed back has the energy $(n-1)J$; the two where the end pair is interchanged have the energy $(n-1)J-3K$; and the remaining $n-8$ have the energy $(n-1)J-4K$. We retain for our set only these $n-8$ terms of energy $(n-1)J-4K$. So we proceed, asking which terms combine with those already set up, and retaining just those whose energy is $-2K$ greater than for those with fewer interchanges. We find that a term of our set, with the energy $(n-1)J-2pK$, has non-diagonal terms to p terms of the set of energy $(n-1)J-2(p-1)K$ and to $(n-3-5p)$ terms of the set of energy $(n-1)J-2(p+1)K$. Evidently so long as p is small, the terms we leave out of the set and yet which combine with terms of the set are comparatively few. It is only for the large p's that we make serious error by leaving out these terms, and for large p the diagonal energy is high enough so that for the lowest states of the perturbed system these unperturbed states are unimportant. Thus we may reasonably believe that the low energy levels found by solving this restricted problem will be approximately some of the low levels of the actual problem. We can at least be sure of the following: by the variation principle, they can be no lower than the actual stationary states.

The other sets of non-combining terms which we can set up are easily described, and are of considerable physical interest. Instead of starting from the state with spins alternating, we start from a state where the spins alternate up to a given point; there the sequence is interrupted, and alternation commences again, so to speak, in the opposite phase, as

$$\cdots \alpha\beta\alpha\beta\beta\alpha\beta\alpha\beta\alpha\cdots .$$

With a few such interruptions in the course of the crystal, the energy is very little above the really lowest state; yet a great many individual interchanges would be required to pass to the lowest state. With such a state to start with, we proceed just as we did before, and construct a whole system of states; and the non-diagonal terms between this and the first system come only from high values of p, involving many interchanges, and can be neglected. Physically, at the interruption of phase, one essentially has a slight interruption of crystal structure. Our catalogue of all possible states of the metal includes not only that where it is one perfect crystal, but also where it is composed of many smaller crystals not perfectly joined together. Obviously each problem can be treated separately; physically it would take a very long time to change from one to the other. And obviously each problem will give us essentially the same set of energy levels.

We now take our set of wave functions, and try to solve the perturbation problem between them. For each value of p, we have many wave functions; and we look for those particular solutions for which all these functions have the same coefficient $S(p)$. Afterwards we shall show that we really find the lowest solutions this way. Then, remembering the number of transitions with non-diagonal term K from a given state, computed above, we have for a typical equation

$$-KpS(p-1)+[(n-1)J-2pK-W]S(p)-K(n-3-5p)S(p+1)=0.$$

This set of difference equations for the S's is somewhat similar to what we had before; it also corresponds to a weighted string. But now the properties, and hence the wave-length, change from point to point, and we seek the various overtones. The equation is a close analogue to Schrödinger's equation, in many ways; the fact that it is a difference equation rather than a differential one is quite immaterial. To solve, we assume $S(p)=e^{\int \alpha dp}$, where α is to vary slowly with p. Then $S(p)=e^{\alpha}S(p-1)$, etc., so that we have

$$-Kp+e^{\alpha}[(n-1)J-2pK-W]-e^{2\alpha}K[n-3-5p]=0,$$

$$e^{\alpha}=\frac{-[(n-1)J-2pK-W]\pm([(n-1)J-2pK-W]^2-4K^2p[n-3-5p])^{1/2}}{-2K[n-3-5p]}.$$

The equation expresses e^{α} as a function of p, for any particular W. Now we must remember that there are essentially boundary conditions; the S's must remain finite for $p=0$ and $p=$an extreme value. To tell how to apply this condition, we must investigate the solution we have found.

The ratio e^{α} of successive coefficients is real or complex, according as $[(n-1)J-2pK-W]^2$ is greater than or less than $4K^2p[n-3-5p]$. Regarded as a function of p, the limiting cases, where the two are equal, come from $(n-1)J-W=2pK\pm 2K[p(n-3-5p)]^{1/2}$. The right hand side, plotted as a function of p, forms an ellipse; the straight line represented by the left side intersects the ellipse in two points, or in none, depending on the value of W. The region of W where it intersects can be found by computing the maximum and minimum ordinates of the ellipse; that is, the values of $(n-1)J-W$ for which $(d/dp)(2pK\pm 2K[p(n-3-5p)]^{1/2})=0$. This gives $p=(n-3)/10$ $[1\pm(1/6)^{1/2}]=(n-3)\times(0.0592, 0.1408)$. At these two limits, substituting, $W=(n-1)J+(n-3)K\times(0.290, -0.690)$. For values of W between these limits, there is a range of p for which e^{α} is complex, and the solution is oscillatory; outside this region, which is closed, the solution is in any case exponential. To satisfy our boundary conditions, now, we have a problem much like that with Schrödinger's equation in one dimension; and boundary conditions can be satisfied only if there is an oscillatory region. As a result, the actual energy levels of the problem must lie between the limits given. Closer examination shows that a "quantum condition" can be applied, and that between these limits there are just the number of energy levels there should be. We now have the lowest level: it lies arbitrarily close to our lower limit, or is

$$W=(n-1)J+0.290(n-3)K,$$

as we stated in the last section. In this lowest state, we can show without trouble that the unperturbed wave functions with p near $0.0592(n-3)$ are represented most strongly. Thus the value of p is really quite small; relatively few pairs are interchanged, and we are safely in the region where we can treat the different systems separately.

We have solved our problem for the lowest state in which all terms of the same p have the same coefficient. We can now investigate the effect of removing this assumption, varying the coefficient of one function of a given p in one direction, varying the rest to keep the same total representation for functions of this p, and calculating the change in the energy. When we do this, we find the energy to be a minimum with respect to such variation; in fact, the changes of energy compensate each other to a higher order, showing that the problem is nearly degenerate with respect to these coefficients. Thus we may be rather confident that we have a good approximation to the lowest non-polar states. It is of course obvious that this method becomes worse as we go to higher states.

It is instructive to ask what ordinary perturbation theory would give us for the lowest state. The lowest unperturbed state has the diagonal energy $(n-1)J$; this represents the ordinary first order perturbation calculation. Now we pass to the second order calculation. The lowest state is not degenerate, so that we can use the power series development method. The next term in the expansion is $\Sigma_j(H_{ij}H_{ji})/E_1-E_j)$, summed over all excited states j. Now there are non-diagonal terms H_{1j} only to the $n-1$ states with $p=1$.

Thus the H_{1j}'s are all equal to $-K$, and the energy differences are all given by $E_j=E_1-2K$. Thus we have as second approximation

$$W=(n-1)J+(n-1)\frac{K^2}{2K}=(n-1)J+\frac{1}{2}(n-1)K.$$

This differs from our result in having the factor $\frac{1}{2}$ rather than 0.290; we have only the first term of a series development, but it is reassuring that agreement is as good as it is. For finding the order of magnitude, we could use this term alone; we shall find this simple method useful with the space lattice.

Effect of polar states. One can make an estimate, by a method like that used here, of the effect of the polar states in depressing the non-polar ones, which alone we have considered so far. We can build up a series of states by starting with a given non-polar state; then removing one of the electrons to an adjacent atom, producing a positive and a negative ion; then removing a second; and so on. The series of states so found behave formally like those used above. If we solve the problem by the previous method, or by the second order perturbation method, we get a further depression of the lowest state, which again can be written as

$$(n-1)\times\sum\frac{\text{square of non-diagonal term}}{\text{energy difference}}.$$

The non-diagonal term which comes in here is presumably of the same order of magnitude as before, although it is a somewhat different integral. But the diagonal energy difference is now essentially an ionization energy, which is of the order of several volts, rather than the fraction of a volt that K is. Thus the effect on the energy is a number of times smaller than what we found before, and we can neglect it. It is not worth while calculating more accurately, in this approximation; for with H_2, it appears that on account of the lack of orthogonality of the wave functions, the actual depression of the energy is very much less than this rough method would indicate, although the effect on the wave function is about what we should expect. One can reasonably believe for this reason that the polar states in the crystal depress the energy only very little. But we recall that their effect on the wave function is to introduce free electrons. By our rough method described above, we infer that the fraction of free electrons is of the order of 1 percent, for reasonable choice of the constants. This could easily be in error by a factor of 10 either way; but at least we see that a definite meaning can be attached to the number of free electrons, and that there is a definite procedure for calculating this number.

Normalization and orthogonality. We have not considered the lack of orthogonality of the wave functions, resulting in factors like the $1/1\pm S$ of Heitler and London. When one tries to do this, one immediately strikes a difficulty which appears insurmountable: the factor in the denominator, instead of being like $1+S$, is like $1+nS+\cdots$, where n is the number of

atoms, so that the term nS is enormous compared with unity. On examination of simple cases, it appears that the remaining terms, coming from other permutations than the simple interchange, are also important, in many cases the terms almost cancelling each other. Further, in every expression for energy, like the simple $(J \pm K)/(1 \pm S)$, there are more terms in the numerator, also of great importance. But the simple cases give no suggestion of how to treat the general case. The key to this difficulty comes from Bloch's method. For example, the term of maximum multiplicity has one function, which can be expressed either by Heisenberg's or Bloch's functions. But the difference is that Bloch's functions are really orthogonal, unlike Heisenberg's, so that we meet no such difficulty. Of course, the same terms occur, but now in the normalization of the individual functions. And the numerators, and denominators like $1+nS+\cdots$, appear as products of n factors, each of approximately a simple Heitler and London form; further, all but one or two of these factors of the denominator cancel against equal factors in the numerator, giving very simple results. Essentially the same method can be used with the other states; for this method is one for treating a determinant of Heisenberg's wave functions, and converting it into a determinant of Bloch's functions; and all of our wave functions are products of two such determinants. When we calculate in our case, it appears that the terms S will have small effect; we are roughly half way between the cases $1+S$ and $1-S$, and the effects of S nearly average out. This method at the same time gives the proper way of considering more distant pairs, as well as adjacent ones; these contribute the further terms in the numerators, as $J \pm K + \cdots$. We see from the next paragraph that these more distant pairs are really quite important.

Method for space lattice. So far, we have spoken about a linear lattice of atoms, rather than a space distribution. We now extend this theory to a crystal; but we shall not carry it through in the same detail. We consider only the problem of zero spin, and use our second order perturbation approximation. Let us take the body-centered cubic lattice, which the alkalies have. The lowest unperturbed state of this lattice can be set up much as with the linear one: we let the electrons at the corners of the cubes have the spin α, those at the centers the spin β. Then each electron is surrounded by eight others of opposite spin, so that if we consider only adjacent pairs, the diagonal energy of this state is $4nJ$, where there are n electrons, $4n$ pairs. This lowest state now has non-diagonal terms, each equal to $-K$, to the $4n$ states obtained by interchanging an adjacent pair. Each of these states has two misplaced spins, each surrounded by 7 spins of the same sign, so that the energy has a term $-14K$. Thus for our perturbation problem, we have a non-diagonal energy $-K$, an energy difference $14K$, and $4n$ non-diagonal terms, so that the perturbed energy is $4nJ+(4nK^2/14K)=4nJ+(2/7)nK$.

This formula is rather significant. We compare the energy with that of the lowest state of the diatomic molecule, $n=2$, which is $(n/2)J+\frac{1}{2}nK$. We observe that for the crystal the coulomb interaction, the term J, has a coefficient eight times as great: each atom has eight neighbors instead of one, each

penetrating. On the other hand, the valence term K has a coefficient only 2/7, instead of 1/2. The valence, so to speak, is spread out among all the neighbors, and weakened in the process. It is partly on this account that we can say that the coulomb interaction is the more important part of the cohesive force, in metals.

We have considered only those pairs with smallest separation, and they give a definite attraction. But in this lattice, there are not only the eight nearest atoms at distance R; there are also six, in directions parallel to the edges of the cube, at distance of $1.155R$, and these have parallel spins, producing therefore a repulsion. In the diagonal energy, each pair will then contribute an energy $J-K$, a positive amount, so that the diagonal energy of the lowest state if $4nJ+3n(J(1.155\ R)-K(1.155\ R))$. The next higher diagonal energy also will differ from this not merely by $-14\ K(R)$, but also by an amount $12\ K(1.155\ R)$, because by interchange of two spins some of these repulsive terms are removed. Thus the lowest energy level, counting also these pairs, is

$$4NJ(R)+3n(J(1.155R)-K(1.155R))+\frac{4nK^2(R)}{14K(R)-12K(1.155R)}\cdot$$

This results, on computation, in a much weakened attraction. If we were to consider in succession the effects of pairs at greater and greater distance, we should come in succession to attracting atoms with antiparallel spin, and repulsive ones with parallel, so that the successive approximations to the energy would oscillate, falling first above, then below, the true value.

Application to sodium. For the sodium crystal, approximate calculations have been carried out, to test these formulas. These were made by taking a simple analytical expression for the wave function of the valence electron of sodium, and computing the integrals J and K. The details of the calculation will not be given here. The first thing that one notices is that, for Na, J is several times larger in proportion to K than in hydrogen. It is this fact, taken together with the increased coefficient of the J term, that results in the importance of the coulomb term. It is also significant in connection with the question, why do the alkalies, and metals in general, form metallic lattices, while hydrogen does not? We can see the essential answer from our energy formulas of the previous page. For substances where J is the important term, the coefficient of J will be greater, and the energy lower, for the crystal than for the same number of atoms in diatomic molecules, and the crystal will be the stable form. For hydrogen, on the other hand, the valence term K is the important one. Here the coefficient in the molecular form is greater; and even if the metallic form of such a substance were stable in the sense of having a minimum of energy for some definite size, as seems quite possible, still the energy in the molecular state would be lower. The atoms in the crystal would tend to form pairs, resulting in a molecular lattice; the molecules would repel each other, and would be held together only by van der Waals forces, which have been neglected in this paper. This seems to be exactly what hydrogen does.

The numerical values for Na are approximately as follows. If we take only the adjacent pairs, the minimum comes at $R=4.9a_H$ approximately, rather seriously less than the correct value 7; this can partly be explained by the observation that the best atomic wave function for use in the crystal would be more extended than that determined from the free atoms, which are here used. The energy at this point comes out about -40 kg cal/gm mol, the coulomb term supplying about four fifths of this; the observed heat of vaporization is 26.4 kg cal, so that this gives, as we should expect, too large a value. If now we consider the repulsive pairs at distance of 1.155 R, the situation is quite changed. In the first place, the energy is reduced from -40 to about -9 kg cal. When we remember that these two values are the first two terms of a series, whose value oscillates on both sides of the answer, it seems very reasonable that the final result should be not far below the experimental value. The problem of properly computing this energy must be done by the method, using Bloch's functions, described in the preceding section. In the next place, the minimum of the curve is greatly broadened: for quite a range of values, from $R=4.9$ (the previous minimum) to $R=7$, the energy stays about constant, the change of the attractive term being just about balanced by the relatively more rapid change of the smaller repulsive effect. (For smaller R's, a situation can be found when the denominator $14\ K(R)-12\ K(1.155\ R)=0$, so that the function becomes infinite; but this is without physical significance.) No doubt a persistence of this effect in the final answer helps to correct the improperly low grating space we have already found. It also is interesting in connection with the compressibility. The alkalies are remarkably compressible, and if we compute the compressibility for the case where only adjacent pairs are considered, the result is too small by a factor of 2 or 3. On the other hand, considering the next set of atoms, our very broad maximum would give much too great a compressibility. Here again it seems that our result may oscillate, perhaps approaching eventually something near the right value.

THE STABILITY OF METALLIC CRYSTAL LATTICES*

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(Received January 22, 1930)

Abstract

The first sections of this paper are a partial repetition and amplification of Born's theory of homopolar crystal lattices, without, however, making any assumption about the law of force between atoms other than that the force is central and that diatomic molecules are possible. The mathematical work is supplemented with graphical illustrations. If the lattice is in equilibrium as regards (*a*) displacement of one atom, (*b*) unidirectional extension of the entire lattice, and (*c*) simple shear of the entire lattice, it is shown that each of these postulates leads to a restrictive condition on the symmetry and pattern of the possible lattices, thus accounting for the high symmetry actually observed. Finally if the equilibria *a*, *b*, *c*, are stable, there are three series of terms in W'', corresponding to elastic constants, which must be positive. Making use of these series, it is shown that the lattice is likewise in equilibrium against motion of one portion *en bloc* relative to another portion and hence that "mosaic" crystals cannot be configurations of minimum potential energy.

Introduction

THE primary purpose of this paper is to determine whether there is any theoretical basis for the existence of a mosaic structure in crystals of metals or other crystals containing atoms of only one kind. This periodic inhomogeneity for which "mosaic" seems the best short equivalent, has been proposed by various workers[1] as accounting for the non-agreement between calculated and observed tensile strengths of crystals.

Zwicky[1] and his collaborators, e.g. Evjen,[3] have made numerical calculations of the energy changes due to the formation of these mosaic structures in ionic lattices, and find that they are to be expected. Zwicky[2] has also published a general thermodynamic proof intended to apply to crystals of any kind, which the writer[4] has criticized. The subject will be dealt with more fully in the closing paragraphs of this paper.

The present paper is an attempt to deal with the same problem, for metallic lattices only, in a rigorous manner.

The preliminary steps are elementary and a recapitulation of other work; but it is hoped that this feature may be of some value to others who have found Born's[5] classical treatment "nicht ganz einfach zu lesen." The method and notation here introduced will be used by the writer in other papers.

* Published by permission of the Navy Department.
[1] Notably Zwicky, Phys. Zeits. **24,** 131 (1923).
[2] Zwicky, Proc. Nat. Acad. Sci. **15,** 11 (1929).
[3] Evjen, Phys. Rev. **34,** 1385 (1929).
[4] Canfield, Phys. Rev. **35,** 1 (1930).
[5] Born, "Atomtheorie Des Festen Zustandes," Leipzig, 1923.

FUNDAMENTAL STATEMENTS

Let us regard the atoms of a homopolar lattice as centers of mutual forces. Whatever wave-functions are in the background of this behavior we do not enquire. Neither do we concern ourselves with whether or not the atoms are charged. We merely assume that all the atoms are alike and that each two of them exert mutual forces on each other, independent of the presence of other atoms, such that at great distances they attract, and at very small distances they repel each other. At very great distances the force of attraction, and all its derivatives, vanishes. Finally, the mutual force has a potential.

We then represent the mutual energy W of two atoms in terms of their distance r by a curve like Fig. 1. In the absence of kinetic energy the two atoms will form a molecule, their centers being at a distance r_e. If they possess relative kinetic energy less than W_e, they will execute vibrations, the amplitude being represented by ρ. Due to the energy curve not being in general a parabola (i.e. not obeying Hooke's Law), these vibrations are neither iso-

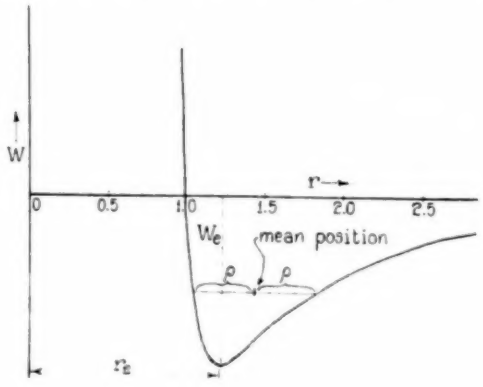

Fig. 1.

chronous nor simply harmonic. The theory of the vibration of such an anharmonic oscillator is part of the theory of molecular spectra.

Our present problem is the application of this energy curve to those polyatomic molecules called crystals.

We next picture an aggregation of atoms in space occupying the points of a regular geometric space lattice and forming a crystal. For the time being we are not concerned with the exact configuration of this lattice. We fix our attention on a single atom of this lattice. We now construct spherical surfaces with this atom as center, such that all of the surrounding atoms fall on one or another of these surfaces. We select some distance, say the distance to the nearest neighbor atom, as a parameter and call it r_0. The number of atoms at the distance r_0 we call $2n_1$. We designate the shells in the order of their radii by subscripts 1, 2, $\cdots$, and their radii by k_1r_0, k_2r_0, $\cdots$ k_ir_0; the number of atoms in the ith shell is $2n_i$.

Referring now to Fig. 2, an energy diagram for our selected atom, we put on it the ordinates corresponding to the various groups of neighbors at dis-

tances $k_i r_0$ and label each ordinate with the corresponding n_i. (It is plain that since the energy of each pair of atoms is W_i, the energy of each atom due to its neighbors at $k_i r_0$ is only $n_i W_i$ instead of $2n_i W_i$). Then the energy of one atom in the lattice is

$$U = \sum_{i=1}^{i=\infty} n_i W_i. \tag{1}$$

We may quite simply refer to n_i as the number of *bonds* of length $k_i r_0$ associated with each atom in the lattice.

Still assuming that the *type* of the lattice is fixed, it is next of importance to find how the crystal attains a configuration of a certain density. We are of course assuming that the atoms are at rest. Actually they are in vibratory motion but it can be shown that the amplitude of vibration is small com-

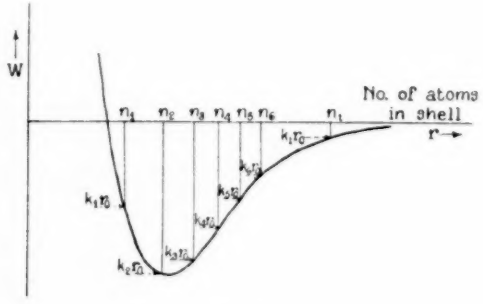

Fig. 2.

pared with r_0 and thus the fixed positions correspond pretty closely with the average positions of the atoms over a period of time. It is plain that a change in r_0 will result in a dilatation of the entire lattice to correspond; the equilibrium configuration will be that for which a small change in r_0 results in no change of energy. We therefore differentiate Eq. (1) as follows:

$$\partial U/\partial r_0 = \sum_i n_i \partial W_i/\partial r_0 = \sum_i n_i k_i W_i' \qquad 0 \tag{2}$$

where $W_i' = [\partial W/\partial r]_{r=k_i r_0}$ and $\partial W/\partial r_0 = k_i W_i'$.

In more graphic terms, the array of ordinates in Fig. 2 is horizontally expanded or contracted, until, each ordinate being weighted with the corresponding number n_i, their sum is a minimum.

It will be of interest at this point to study the diagrams in Fig. 3. Diagram *A* is a plot of the number of bonds of length r or less than r for an atom in a face-centered cubic lattice; diagram *B* for a body-centered, and *C* for a simple cubic lattice. The dotted lines represent the same functions calculated on the assumption of uniformly distributed matter.

Several points of interest are at once apparent. There are almost always more bonds, shorter than any specified length, in a face-centered than in a body-centered cubic lattice, and more in the latter than in a simple cubic. It

is just this characteristic that is implied by the words "close-packing" applied to the two former types. Thus if atoms were rigid spheres attracting each

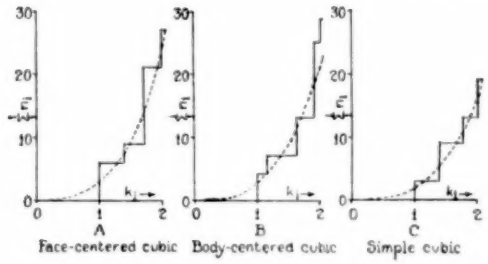

Fig. 3

other according to an inverse power of r, and therefore possessing an energy curve like Fig. 4, they would inevitably choose one of the configurations of

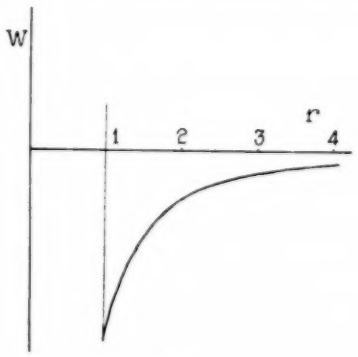

Fig. 4

closest possible packing, i.e., the face-centered cubic or close-packed hexagonal (practically equivalent).

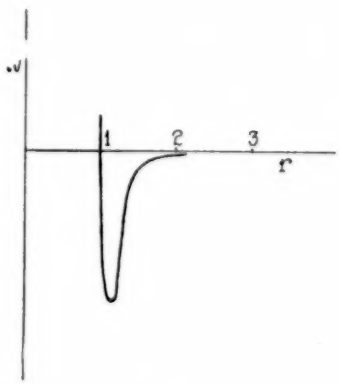

Fig. 5

On the other hand, if the energy curve were like Fig. 5, they would choose the body-centered cubic type, since here there is room for the first two groups

of the body-centered lattice, containing 7 bonds and thus more negative potential energy than the face-centered type, which would have only one group containing 6 bonds in the deep loop of the diagram.

We thus already see a clue to the explanation of the different types of lattices. The expression for dU in terms of the second power of dr_0 yields a formula for the compressibility of the crystal. This is of course positive, since the configuration is one of stable equilibrium. The expression is

$$dU = \tfrac{1}{2} dr_0^2 \sum n_i k_i^2 W_i''.$$

Equilibrium Against Various Displacements

1. *Displacement of a single atom.* We have already established the manner in which the atoms place themselves on a lattice of a certain type and with a certain density, i.e., equilibrium as regards dilatation and change of lattice type. It is next in order to study equilibrium against a displacement of one atom from its correct position, for if the lattice is not in stable equilibrium against such displacements, thermal agitation will destroy it. Referring to

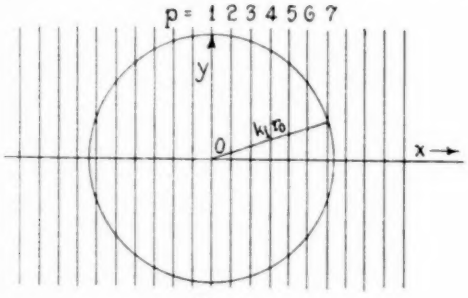

Fig. 6

Fig. 6, the atom O under consideration is shown at the center of the ith sphere. Atom O suffers a displacement dx. The atoms in the shell i are arranged in groups p for which all the atoms in any group p lie in the same plane perpendicular to x. The number of atoms lying in the pth plane of the ith shell is n_{ip} and their bonds to O all make the same angle θ_{ip} with the X-axis. Evidently $\Sigma_p n_{ip} = 2n_i$. The change in energy dU due to the motion dx is then (only taking account of the atoms in shell i)

$$dU_i = \left(W_i' \sum_p n_{ip} \cos \theta_{ip} \right) dx.$$

For all the shells i we then have

$$dU = \left(\sum_i (W_i' \sum n_{ip} \cos \theta_{ip}) \right) dx = 0. \tag{3}$$

But we already have an equation (Eq. (2)) of the form

$$\sum_i A_i W_i' = 0,$$

and since these are two linear equations in the W_i' their coefficients must be proportional or else the coefficients of Eq. (3) must be zero. The latter is the only possible alternative* and thus we have for any i,

$$\sum_p n_{ip} \cos \theta_{ip} = 0 \tag{4}$$

as a restrictive condition on the configuration.

Put into words this means that an atom in the lattice must lie at the center of gravity of each of the concentric surrounding shells of atoms. Most, if not all, of the known crystalline elements obey this condition, so that it cannot be called highly restrictive.

Having disposed of the terms involving dx we now develop dU_i in terms of dx.[2] Referring again to Fig. 6, it will be seen that $dU_i = \frac{1}{2}(W_i'' \Sigma_p n_{ip} \cos^2 \theta_{ip}) dx^2$, in which the coefficients of W_i'' are always positive. But W_i'' may be either positive or negative, so we have no *a priori* knowledge of whether ΣdU_i is positive or negative. If negative the lattice is in unstable equilibrium. Since we know, however, that actual lattices are actually in stable equilibrium we have the strongest reasons for believing that

$$\sum_i \left(W_i'' \sum_p n_{ip} \cos^2 \theta_{ip} \right) > 0 \tag{5}$$

and we can hereafter use this series for comparison.

2. *Equilibrium against uniform extension in one direction.* We now assume that the whole lattice is uniformly stretched in the X-direction at the same time not permitting it to contract laterally. Let the amount of stretch per unit length be ϵ. Referring again to Fig. 6, we see that bond ip is stretched an amount $\epsilon k_i r_0 \cos^2 \theta_{ip}$. Hence

$$dU_i = k_i W_i' \epsilon r_0 \sum_p n_{ip} \cos^2 \theta_{ip}$$

where θ_{ip} is now confined to values between $-\pi/2$ and $+\pi/2$. If equilibrium exists

$$\sum_i k_i W_i' \sum_p n_{ip} \cos^2 \theta_{ip} = 0.$$

Comparing the above expression with Eq. (2) as before, it is plain that we have the same two alternatives; but since the coefficients of W_i' in the above expression are definitely positive, each one must be the same multiple of the corresponding coefficient in Eq. (2), i.e.

$$\sum_p n_{ip} \cos^2 \theta_{ip} = a n_i \tag{6}$$

where a is the same constant for every different value of i, but not the same for different directions of the axis of elongation.

This result may be put into more familiar terms by saying that the planar moment of inertia of every shell of atoms with respect to a given YZ plane is

* For $\Sigma_p n_{ip} \cos \theta_{ip} \leqq n_i$, while n_i becomes a smaller and smaller fraction of $k_i n_i$.

the same fraction of $k_i^2 r_0^2 n_i$ for that shell. In particular it will be noticed as a result of familiar properties of moments of inertia, that the principal axes of inertia have the same directions for all shells, and the principal moments of inertia are in the same proportion. This constitutes a very severe restriction on the pattern of the lattice.

The terms in ϵ^2 are now to be evaluated. By a similar reasoning to that employed in the previous paragraphs, we find

$$dU_i = \tfrac{1}{2} W_i'' k_i^2 \Big(\sum_p n_{ip} \cos^4 \theta_{ip} \Big) \epsilon^2 r_0^2$$

or

$$dU = \tfrac{1}{2} \epsilon^2 r_0^2 \sum_i k_i^2 W_i'' \sum_p n_{ip} \cos^4 \theta_{ip}$$

and since we have experimental evidence that crystals are in stable equilibrium against just such an extension as this, we are justified in concluding that

$$\sum_i k_i^2 W_i'' \sum_p n_{ip} \cos^4 \theta_{ip} > 0. \tag{7}$$

The series in Eq. (7) is proportional to the elastic constant c_{11} for the X-axis we have selected.

3. *Equilibrium against shear.* Imagine the lattice distorted parallel to the XY plane, the displacements being given by $dy = \epsilon x$, $dx = 0$, $dz = 0$. This is a simple shearing distortion. The first order terms in the energy-change are of the type

$$dU_i = \epsilon r_0 k_i W_i' \sum_p \cos \theta_{ip} \sin \theta_{ip} \sum_q \cos \phi_q$$

where ϕ_q is the angle between the XY plane and the plane through the X-axis which contains the atom in question, and where the summation with respect to q means summation over the atoms lying in the circle of intersection of the plane p and the shell i. This expression may be rewritten:

$$dU_i = \frac{\epsilon W_i'}{k_i r_0} \sum_r x_r y_r$$

where the summation is over the atoms of the ith shell. For all the shells:

$$dU = \epsilon r_0 \sum_i k_i W_i' \sum_r \frac{x_r y_r}{k_i^2 r_0^2}$$

and if this latter expression equals zero we have:

$$\sum_i k_i W_i' \sum_r \frac{x_r y_r}{k_i^2 r_0^2} = 0.$$

Comparing this equation with Eq. (2) as before, we find the two only compatible if

$$\sum_r x_r y_r = f n_i k_i^2 r_0^2 \tag{8}$$

where f is the same constant for each value of i, but varies with the orientation of the coordinate frame. It turns out that Eq. (8) is a consequence of Eq. (6), as a simple calculation will demonstrate. Thus, equilibrium against shear introduces no restriction on the lattice geometry beyond what was already imposed by the equilibrium against unidirectional elongation. (This might have been directly inferred from the theory of elasticity).

The expression for dU in terms of ϵ^2 must be greater than zero if the equilibrium against shear is stable. The corresponding inequality is:

$$\sum_i k_i^2 W_i'' \sum_p \sin^2\theta_{ip} \cos^2\theta_{ip} \sum_q \cos^2\phi_q > 0. \tag{9}$$

The series in Eq. (9) is proportional to the elastic constant c_{66} for the axes selected.

4. *Equilibrium against displacement of a large portion of the lattice.* The principal object in deriving the equations of the preceding paragraphs was not to prove that crystals can exist, for we know this from observation, but to obtain certain series in W_i' and W_i'' of which the sums are known to vanish, or be positive respectively, and which can be used for comparison with other series in W_i' and W_i'' of which the behavior is not known from observation.

We now draw another picture of our lattice, Fig. 7, in which we once more show all the atoms lying on a series of equidistant planes, each plane

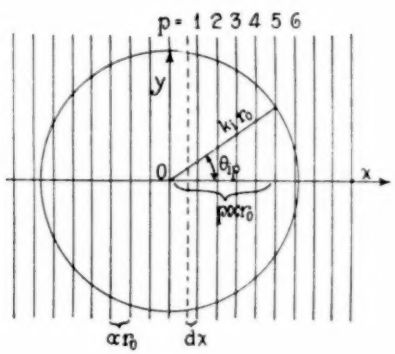

Fig. 7.

containing an equal number of atoms. (For some lattices the planes may not be equidistant, or equally densely packed, but there will always be a repetition of the same distances in the same order, and the argument is but little affected). The X-axis is an arbitrary line in space as before. Though the transverse planes may be very close together and contain each but a few atoms, nevertheless the lattice can always be resolved into such a series of planes with finite separation and perpendicular to an arbitrary axis. The distance between planes is αr_0.

Now we elect to remove the portion of the lattice lying to the right of 0 by a distance dx from the portion to the left. In so doing we elongate every bond crossing the gap dx by an amount $dx \cos\theta_{ip}$.

We must also notice that if $k_i \cos\theta_{ip} = \alpha$, only the atoms lying in the plane through 0 have their bonds affected. But if $k_i \cos\theta_{ip} = 2\alpha$, then the plane through 0 and also its neighbor on the left contain atoms whose bonds are lengthened; and in fact if $k_i \cos\theta_{ip} = p\alpha$ there are p planes to the left of 0, and including 0, containing atoms whose ith bonds are lengthened by the operation. So if there are N atoms in each plane

$$dU_i = NW_i' dx \sum_p n_{ip} p \cos\theta_{ip}$$

But $p = k_i \cos\theta_{ip}/\alpha$ hence

$$dU_i = \frac{Nk_i W_i' dx}{\alpha} \sum_p n_{ip} \cos^2\theta_{ip}$$

and

$$dU = (Ndx/\alpha) \sum_i W_i' k_i \sum_p n_{ip} \cos^2\theta_{ip} \tag{10}$$

where θ_{ip} takes on values between $-\pi/2$ and $+\pi/2$.

But Eq. (6) told us that $\Sigma_i[W_i' k_i \Sigma_p n_{ip} \cos^2\theta_{ip}] = 0$. Hence in Eq. (10) $dU = 0$. Hence the lattice is in equilibrium against the assumed displacement.

We now develop dU in terms of dx^2 as follows:

$$dU_i = \frac{1}{2} Ndx^2 W_i'' \sum_p n_{ip} p \cos^2\theta_{ip}$$

$$= \frac{1}{2} \frac{Ndx^2 W_i'' k_i}{\alpha} \sum_p n_{ip} \cos^3\theta_{ip}$$

whence

$$dU = (Ndx^2/2\alpha) \sum_i k_i W_i'' \sum_p n_{ip} \cos^3\theta_{ip} \tag{11}$$

The question whether the equilibrium we have been discussing is stable depends on whether the series in Eq. (11) is positive.

To settle this matter we shall require the series of Eq. (7) for purposes of comparison. Let us use the letter S for the latter series and the letter S' for the series of Eq. (11). If we now refer to Fig. 2 we see that for the first few terms W_i'' is positive, and for all the remainder out to infinity W_i'' is negative. Let us say that W_μ'' is the last positive term. Then we may write $S = S_A - S_B$ where S_A is a terminating series ending with W_μ'', and S_B is an infinite series of positive terms starting with $-W_{\mu+1}''$. The fact that $S > 0$ implies that $S_A > S_B$. Similarly we divide S' into two parts S_A' and S_B' the division being at the same term as for S. Let the i term of S be S_i and the i term of S' be S_i'. Then

$$\frac{S_i}{S_i'} = \frac{k_i^2 W_i'' \sum n_{ip} \cos^4\theta_{ip}}{k_i W_i'' \sum n_{ip} \cos^3\theta_{ip}}$$

$$= \alpha \cdot \frac{k_i W_i'' \sum p n_{ip} \cos^3\theta_{ip}}{k_i W_i'' \sum n_{ip} \cos^3\theta_{ip}} .$$

Let $S_i/S_i' = t_i$. Evidently $\alpha < t_i < \alpha q_i$ where q_i is the largest integer in k_i/α, i.e., the largest value of p. Also $t_i < t_{i+1}$.*

We may now write the two series as follows:

$$S = S_A - S_B = \sum_1^{\mu} t_i S_i' - \sum_{\mu+1}^{\infty} t_i S_i'$$

$$S' = S_A' - S_B' = \sum_1^{\mu} S_i' - \sum_{\mu+1}^{\infty} S_i'.$$

Then

$$\alpha < S_A/S_A' < t_\mu < \alpha q_\mu \gtrless \alpha q_{\mu+1} < S_B/S_B'.$$

or

$$S_A/S_A' < S_B/S_B'.$$

But

$$S_A > S_B$$

hence

$$S_B/S_A' < S_B/S_B'$$

or

$$S_A' - S_B' > 0.$$

The expression in Eq. (11) is therefore positive, and the equilibrium is stable. In other words, any displacement of a portion of the perfect lattice directly away from another portion sets up a restoring force. If the crystal does not extend to infinity to right and left, the effect will only be to make S_B and S_B' terminating series, and the inequalities will be even more pronounced. It only remains to carry through a similar argument with respect to a lateral displacement of one portion of the lattice relative to the other. It turns out that, using a similar notation and procedure to that which preceded,

$$S = \sum_i k_i^2 W_i'' \sum_p \cos^2 \theta_{ip} \sin^2 \theta_{ip} \sum_q \cos^2 \phi_q \qquad \text{(Eq. 9)}$$

$$= \alpha \sum_i k_i W_i'' \sum_p p \cos \theta_{ip} \sin^2 \theta_{ip} \sum_q \cos^2 \phi_q$$

and

$$S' = \sum_i k_i W_i'' \sum_p \cos \theta_{ip} \sin^2 \theta_{ip} \sum_q \cos^2 \phi_q.$$

From which, as before, we find that $dU > 0$ and the equilibrium is stable with respect to this displacement too.

Possible Classes of Symmetry in Homopolar Crystals

In this section we shall discuss rather briefly the consequences of Eqs. (4) and (6), so far as they affect the symmetry properties of homopolar lattices as defined in the opening paragraph.

The meaning of Eq. (4) is that any atom in the lattice must lie at the center of gravity of any group of atoms which are situated on the surface of a

* For large values of k, t approaches $(4/5)\,k$; there may be isolated values of i for which $t_i > t_{i+1}$ but these are very rare. It is impossible to imagine a W function for which this slight departure from rigor would invalidate the general conclusion.

sphere with the atom in question at its center. It is plain that the atoms of such a group must display at least all the elements of symmetry of the crystal as a whole. (They may display additional elements of symmetry, but here we are concerned with minimum requirements.)

The elements of symmetry, so far as they affect our present argument, are: (1) a center of symmetry; (2) an axis of symmetry, either digonal, trigonal, tetragonal or hexagonal; (3) a plane of symmetry. The properties of these as they affect the center of mass are as follows:

1. The center of gravity coincides with a center of symmetry if one exists.
2. Any axis of symmetry contains the center of gravity.
3. Any plane of symmetry contains the center of gravity.

Since all elements of symmetry of points on a sphere contain the center of the sphere, it is sufficient that the elements of symmetry shall determine a point, to make that point the center of gravity. This then may be accomplished in the following ways:

(1) A center of symmetry.

(2) Two axes of symmetry of any order.

(3) An axis of symmetry and a plane of symmetry which does not contain the axis.

(4) Three non-collinear planes of symmetry.

Any class of symmetry, then, which displays at least one of the four combinations of symmetry elements listed above, fulfills the requirements of

TABLE I.†

Class (Dana)	Symbol (Schoenflies)	Class (Dana)	Symbol (Schoenflies)
I. Triclinic System		V. Cubic	
Asymmetric	C_1	*Tetartohedral	T
*Normal	C_i	*Pyritohedral	T^h
II. Monoclinic System		*Tetrahedral	T^d
Clinohedral	C_s	*Plagihedral	O
Hemimorphic	C_2	*Normal	O^h
*Normal	C_2^h	VI. Hexagonal.	
III. Orthorhombic		(Rhombohedral Division)	
Hemimorphic	C_2^v	*24	C_3
*Sphenoidal	V	*Trirhombohedral	C_3^-
*Normal	V^h	Ditrigonal Pyramidal	C_3^v
IV. Tetragonal		Trapezohedral	D_3
Tetartohedral	S_4	*Rhombohedral	D_3^d
*Sphenoidal	V^d	(Hexagonal Division)	
Pyramidal Hemimorphic	C_4	*23	C_3^h
*Pyramidal	C_4^h	*Trigonotype	D_3^h
Hemimorphic	C_4^v	Pyramidal Hemimorphic	C_6
*Trapezohedral	D_4	*Pyramidal	C_6^h
*Normal	D_4^h	Hemimorphic	C_6^v
		*Trapezohedral	D_6
		*Normal	D_6^h

*Indicates classes which conform to barycentric symmetry condition of Eq. (4) in text.
† Table copied from Wykoff: "The Structure of Crystals", N. Y. 1924.

Eq. (4). In Table I are listed the 32 recognized classes of crystal symmetry. Those classes which obey Eq. (4) are designated with asterisks. Of the 32

classes, 21 obey this condition. All the known space lattices of crystal elements fall into the 21 classes with the possible exception of graphite, of which the lattice is still the subject of discussion.

We still have to discuss the consequences of Eq. (6), which imposes a restriction far more severe than Eq. (4).

Eq. (6) demands that the principal axes of inertia of each sphere of atoms concentric with a selected atom shall have the same directions (this also follows from symmetry considerations) and that the principal planar moments of inertia shall be in the same proportion. So far as the writer can determine, this condition is satisfied by the five classes of the cubic system and none other. The hexagonal close-packed arrangement may be said to satisfy the condition 'approximately', i.e. the first departure is in the shell $i=3$, and involves the transfer of two atoms from a shell containing twelve, to a shell of about 6 percent smaller radius. Just what meaning can be attached to this 'approximate' fulfilment of such a condition is not clear. It may mean that this small departure from equilibrium can be balanced by a minute polar force-field superposed on the central force-field which we have postulated in the first paragraph of the Fundamental Statements above.

It may finally be remarked that if Eq. (2) has a solution r_0 for a particular lattice type, and if this lattice type satisfies Eqs. (2) and (4), and if $\Sigma n_i W_i$ is smaller for this configuration than for any of the other configurations satisfying Eqs. (1), (2) and (4), then the inequalities expressed by Eqs. (5) and (7) show that no lattice obtained by a homogeneous deformation of the given lattice can satisfy the given conditions. Moreover, since the validity of these inequalities is only increased by leaving out terms beyond the first few terms in the summations, all departures from complete geometrical perfection in the interior of a homopolar crystal are unstable.

At points near the surface of a crystal, particularly for points nearer to the surface layer than the distance at which $W_i''=0$, the above statement is not true; the writer hopes to make those surface conditions the subject of a future paper.

Mosaic Structures

The displacement of one portion of a crystal *en bloc* relative to the other portion may be said to be the purest type of inhomogeneous deformation. From the two cases of this kind which we have considered above, in conjunction with the postulated stability against homogeneous deformation, it is possible to show that any conceivable picture of inhomogeneous deformation leads to an increase of energy in the second order terms of the displacements. Among others, it is possible to show that the equilibrium is stable against a uniform or non-uniform contraction of a single lattice plane.

Two types of variation from perfect symmetry are conceivable mosaic structures. The first is obtained by some sort of inhomogeneous deformation of an originally perfect lattice. Our conclusions given above show that any such configuration involves a greater energy than the original.

The second is obtained by some such inhomogeneous deformation forming gaps in the lattice into which additional atoms are inserted. To show that this results in a preferred configuration it is necessary not merely to show (a) that the new atom has a negative potential energy greater than the positive energy created by the deformation, but also (b) that the net decrease in energy thereby effected is greater than what would result from adding one more atom in a normal way to the structure of the perfect lattice. Zwicky[6] in replying to the author's[4] criticism his general thermodynamic argument for all crystals, recapitulates his calculations for an ionic lattice (rock salt), and establishes the condition (a) above; but he does not show that condition (b) is satisfied as well.

Evjen[2] has calculated the case of inhomogeneous deformation of a rock-salt lattice and finds as we do here for a homopolar lattice, that the energy terms in the second powers of the displacements are positive. He does, however, find that when terms of the third and fourth powers are included, it is possible to find a secondary minimum in the energy which may be lower than the original minimum.

In concluding the author wishes to express to Professors K. F. Herzfeld and F. D. Murnaghan his appreciation of their comments on certain portions of this paper.

[6] Zwicky, Phys. Rev. **35**, 3 (1930)

THE INFLUENCE OF TEMPERATURE ON POLARIZATION CAPACITY AND RESISTANCE

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(Received January 16, 1930)

Abstract

The temperature coefficients of polarization capacity and resistance have been determined for gold and plain platinum electrodes in 0.63, 1.50 and 2.42 N solutions of sulphuric acid and also at different frequencies for 1.46 N concentration. To reduce the electrodes to a condition representing minimum capacity, a method of thermal treatment was employed and found quite effective. Values of the angle of phase difference have been computed for the various conditions under which measurements were made.

During the process of reducing the electrodes to a condition representing minimum capacity, the value of polarization capacity decreased to about one-half the original value and the resistance increased to a few times the original value. The angle of phase difference increased 15 or 20 degrees. After the electrodes were conditioned, consistent and reproducible values of capacity and resistance could be obtained.

The temperature coefficient of capacity is about twice as great with platinum as with gold electrodes and is apparently independent of concentration. Phase difference changes only slightly with temperature, but increases with concentration. The absolute values of the slopes of the curves, capacity versus temperature and resistance versus temperature, decrease with increasing frequency. The temperature coefficient of capacity, however, increases with frequency for platinum electrodes and decreases in the case with gold electrodes.

THERE has been a limited amount of investigation of the effects on polarization capacity and polarization resistance caused by changes in temperature. Sheldon, Leitch and Shaw[1] determined the temperature coefficient of capacity for cells consisting of Pt $|H_2SO_4|$ Pt and Hg $|H_2SO_4|$ Pt. Schönherr[2] studied the influence of temperature on the reduction of the electrodes to a condition corresponding to minimum capacity. The work herein described was an investigation to determine the nature and magnitude of changes in polarization capacity and resistance as influenced by changes in temperature, under various conditions with respect to the concentration of the electrolyte, the frequency of the applied voltage and the material and condition of the electrodes.

Apparatus and Experimental Procedure

Measurements were made by means of the Wheatstone bridge and auxiliary apparatus, diagrammatically represented in Fig. 1. The low-power vacuum tube oscillator which had a frequency range from 600 to 4000

[1] Sheldon, Leitch and Shaw, Phys. Rev. (1) **2**, 401 (1895).

[2] Schönherr, Ann. d. Physik u. Chemie **6**, 116 (1901).

cycles per second was loosely coupled to the bridge by means of a step-down transformer in order to maintain the voltage across the polarization cell at or below the value corresponding to minimum or initial-capacity. Minimum or initial-capacity is that value of polarization capacity characteristic of the cell when the applied voltage is sufficiently low that further decrease in voltage does not result in any appreciable decrease in the value of polarization capacity. With respect to variations in capacity as influenced by variations in voltage, Wien[3] found that the polarization capacity was constant at the minimum value if the voltage across the cell was 0.05 or less. Wolff[4] found the capacity nearly constant for voltages less than 0.1 volt. In the present work, in order to ascertain whether or not variations in applied voltage were influencing the measurements, the voltage across the polarization cell was measured by means of a vacuum tube voltmeter and was found to be less than the critical value. Also, resistance was inserted in the leads to the bridge without decreasing the measured value of capacity. All values of polarization capacity recorded in this paper are, therefore, thought to be

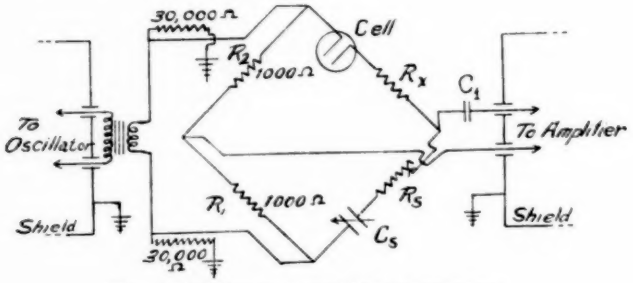

Fig. 1. Bridge and auxiliary apparatus.

minimum values insofar as the influence of the voltage applied to the cell is concerned.

The resistances, R_1 and R_2, in the ratio arms of the bridge were maintained equal in order to minimize the effects of distributed capacity and inductance although with the type of bridge used and at the comparatively low values of frequency, effects of distributed capacity and inductance were negligible. The condenser, C_1, was a fixed condenser and served to prevent any direct current through the cell.

Fig. 2 is a diagram of the polarization cell. The cell consisted of a container in the form of a test tube, with a pair of similar electrodes mounted by inserting through the perforated stopper the glass tubes into which the wire electrodes were sealed. The thermometer was similarly mounted with the center of the bulb in the same horizontal plane as the faces of the electrodes, the thermometer and electrodes being securely fastened together so that the faces of the electrodes were coplanar and about 3 mm apart. The end of any glass tube containing an electrode was ground transversely to the length so that the exposed circular cross-section of the wire electrode was

[3] Wien, Ann. d. Physik u. Chemie **58,** 37 (1896).
[4] Wolff, Phys. Rev. **27,** 755 (1926).

flush with the end of the tube. Gold and plain platinum electrodes were used, the gold having a diameter of 2 mm and the platinum a diameter of 0.623 mm. Under the conditions of the experiment, the capacity of polarization cells with electrodes as described was within the range from 0.03 to 0.7 microfarads and the corresponding range of polarization resistance was from 4000 to 500 ohms. For any particular test the electrolyte was an aqueous solution of sulphuric acid of desired concentration, which had been heated to free it of absorbed gases. The temperature of the cell was controlled by immersing it in an oil or water bath, the temperature of which could be controlled at will.

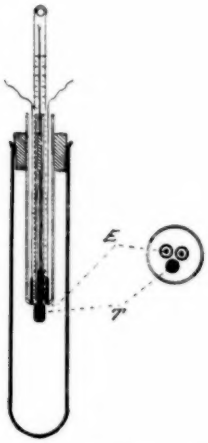

Fig. 2. Polarization cell. *E*, electrode. *T*, bulb of thermometer.

Data were obtained for any one set of conditions by making a series of measurements as the temperature was increased through a range from 0°C to a maximum of 90 or 95°C and then decreased through the same range.

The Effect of Thermal Treatment on Stabilization of the Electrodes

As have other experimenters,[5] the writer found that cells having freshly surfaced electrodes do not give consistent and reproducible values of capacity and resistance. Incidentally, in attempting to duplicate results for rising and falling temperatures of a cell with freshly surfaced[6] electrodes, it was found that the effect of any so-called temperature run such as that described above was to decrease considerably the values of capacity and increase the values of resistance. The value of the capacity at 0°C after the cell had been taken through the range of temperatures was reduced to a value which was from 40 to 60 percent of the original value at that temperature on starting the run. More marked changes took place in the resistance, the final value of which might be as much as four times greater after the conditioning runs. After

[5] Gordon, Göttingen Diss. 72 (1896–97); Orlich, Diss., Berlin (1896); Wolff, reference 4.

[6] The electrodes were surfaced by filing with a fine-grained file.

two or three such runs with a cell, values of capacity and of resistance obtained with falling temperature were in agreement with those obtained with rising temperature. Schönherr,[7] also, found by increasing the temperature of the cell through a considerable range and then decreasing it through the same range that the final value of capacity was much less than the original value.

The manner in which polarization capacity and resistance change for freshly surfaced platinum electrodes when the cell is subjected to a series of runs is shown by the curves of Fig. 3. Curve A shows the relation between capacity and temperature for the initial run and curve B shows the relation

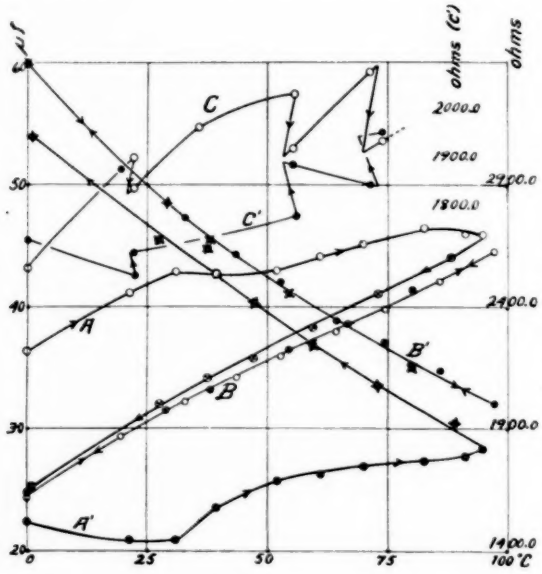

Fig. 3. Capacity-temperature and resistance-temperature curves for platinum electrodes while in the process of being conditioned. For explanation of curves, see text. Values of capacity are in microfarads per sq cm for one electrode and the plotted values of resistance represent total resistance of the cell. To obtain resistance per sq cm for one electrode, the values as plotted should be multiplied by 0.0015. Open circles, without and with crosses, represent values of capacity for increasing and decreasing temperature, respectively, while filled-in circles represent values of resistance, circles with projections being values obtained with decreasing temperature. For all curves, the concentration was normal and the frequency was 1020 cycles per second.

for the third run, the second having given results nearly the same as the third. The corresponding curves showing the development of polarization resistance[8] are A' and B', respectively. It may be noted in curve B (capacity)

[7] Schönherr, reference 2.

[8] Values of resistance are in all cases the measured values of the total resistance of the polarization cell without deducting for the resistance of the electrolyte which was assumed negligibly small in comparison with the resistance of polarization. A test of the validity of this assumption was made by varying the spacing between the electrodes and noting the effect on resistance. When the spacing was increased to 16 times the original value, the resistance

and in curve B' (resistance) that the agreement between the values of capacity and of resistance for rising temperature and the corresponding values for falling temperature is reasonably good. This same fact is also well emphasized in the curves of Fig. 4, in nearly all of which the values obtained with rising temperature are in very good agreement with those obtained with falling temperature. The one prominent exception in the curves of Fig. 4 is in the case of curves C (capacity-temperature for 0.63 N solution, with plain platinum electrodes) and C' (the corresponding curve for resistance). The lack of agreement in this case is due to the fact that these curves represent the first run of the series with the platinum electrodes and there had been only one run made to condition the electrodes previous to taking the data for these curves. The one run was not sufficient fully to condition the electrodes. In fact, in curves B and B' which are plotted from measurements made during a run following that for curves C and C', there is still lack of complete agreement between the rising and falling-temperature branches of the curves.

When cells with gold electrodes were treated similarly, the effect was similar, excepting that the gold electrodes were more readily conditioned and did not require as many conditioning runs as did the platinum electrodes.

Success in duplication of results in making measurements of polarization capacity and resistance was possible only when the electrodes were fully conditioned. The writer found the method of thermal treatment as described above to be quite effective in accomplishing this and it is, moreover, a method which requires much less time than that of leaving the electrodes in the electrolyte to age for several days. Just what the condition of the electrode is when it has minimum capacity for a given set of conditions, is not definitely known. It doubtless represents a certain condition with respect to absorbed gas and also with respect to the condition of the surface. As have other experimenters, the writer observed that the electrodes undergo a change in color as they become conditioned, changing from a bright to a dull color. It was also observed that the electrodes could be conditioned in an electrolyte of given concentration and then be used in an electrolyte of different concentration and yet have capacity according to the second concentration.

In curves A and A', Fig. 3, on the rising-temperature branches of the curves, attention is called to the fact that at a temperature of about 31°, the capacity underwent a rather sudden decrease and the resistance a sudden increase. The cause for these changes was a drop of about 1° in the temperature of the cell at this point after which, although the temperature was

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increased only 3.5 percent. Also, the platinum electrodes which were used during the experimental work were finally platinized and the total resistance was determined. The value thus determined, when corrected for concentration, was not in any case more than 5 percent of the total resistance of the cell with plain platinum electrodes. Since part of the resistance of the cell as measured with platinized electrodes was resistance of polarization for platinized platinum, the value of the resistance of the electrolyte thus determined was somewhat too large. Consequently, 5 percent is a liberal estimate of the outside limit of the approximation.

again brought to its former value, the values of capacity and of resistance had undergone the changes noted. Later, in order to investigate this effect further, the electrodes were again freshly surfaced and the data represented in curves C and C' were obtained. In taking the data for these curves, the temperature was purposely permitted to fall 1 or 2 degrees at three different points on the ascending parts of the curves. The curves show that apparently the reversal of the temperature gradient with reference to the electrode and the electrolyte is effective in decreasing the capacity and increasing the resistance and also that a change in capacity is accompanied by a corresponding and closely related change in resistance.

During the conditioning process in case of the cell with platinum electrodes the phase difference, i.e., $\tan^{-1}\omega RC$, where ω is $2\pi\times$frequency, R is polarization resistance and C is polarization capacity, increased from 27° to 40° and in case of the cell with gold electrodes the phase difference increased from 12° to 35°. The initial low value of phase difference in the latter case is probably due to the fact that the gold electrodes had previously been heated to the melting point, while in the case with the platinum electrodes, the electrodes had been freshly surfaced by filing, only. The electrode, then, having the property of polarization capacity, may be regarded as becoming a less perfect condenser as the electrode becomes conditioned or as it acquires the condition corresponding to minimum capacity.

The writer has chosen in this paper to regard polarization capacity and the resistance associated with it as being equivalent to a pure capacity and a pure resistance in series. Successful attempts were made, however, to balance the bridge both with a resistance in series with a mica condenser in the arm of the bridge opposed to the polarization cell, and also with a resistance in parallel with the standard condenser. The results were as follows:

Measured values of capacity and resistance when the cell was balanced by a capacity and resistance in series were, respectively,

$$0.0515\ \mu f \text{ and } 2840 \text{ ohms.}$$

When C_m and R_m, signifying the corresponding values for the multiple relation, are computed from the above values,

$$C_m=\frac{C_s}{1+\omega^2C_s^2R_s^2}=0.0274\mu f$$

and

$$R_m=R_s\left(1+\frac{1}{\omega^2C_s^2R_s^2}\right)=6070 \text{ ohms.}$$

The values of C_m and R_m as measured directly by means of the bridge were, respectively, 0.0292μf and 5920 ohms, in reasonably good agreement with the computed values. The balance or null point was quite distinct in both cases.

Temperature Coefficient and Concentration of the Electrolyte

With gold and plain platinum electrodes, conditioned according to the method described above, data were taken for different concentrations of the electrolyte as the temperature was varied over the complete range. The data so obtained are plotted in the curves of Fig. 4, the variation of capacity and

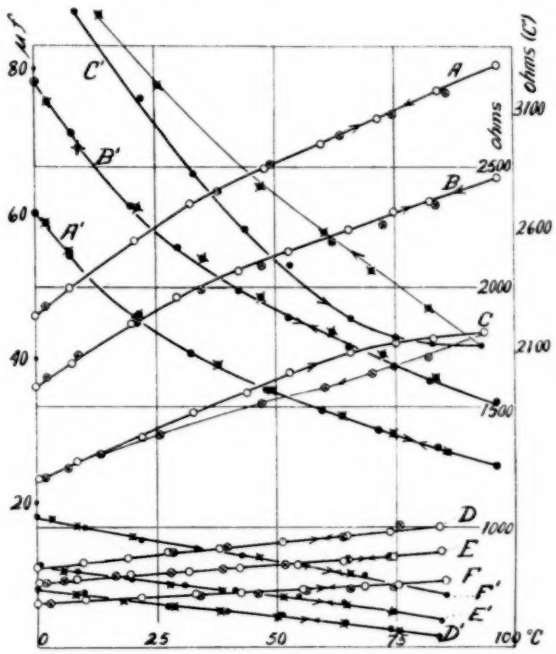

Fig. 4. Curves, capacity-temperature (letters not primed) and resistance-temperature (corresponding, primed letters) for different concentrations of the electrolyte. Curves A, A', D and D' are for 2.42 N concentration; curves B, B', E and E' are for 1.50 N; and curves C, C', F and F' for 0.63 N. The six upper curves are for platinum electrodes and the six lower for gold. For the significance of different kinds of points, see explanation, Fig. 3. The frequency was constant at 1000 cycles per second. All values of capacity are in microfarads per cm^2 for one electrode, but values of resistance represent the total resistance of the cell. To obtain resistance per cm^2 for one electrode, the plotted values should be multiplied by 0.0015 for the cases with platinum electrodes and by 0.0174 for the cases with gold electrodes.

the corresponding variation of resistance with temperature for the three different values of concentration being shown for the two kinds of electrodes.

Table I shows results of computations based on the curves of Fig. 4 and the data relating thereto. As is indicated in the table, the temperature coefficient of capacity, defined as

$$(1/C_{18})(dC/dT)_{18},$$

is about twice as much for platinum electrodes as for gold, other conditions being the same. With possibly an exception in the case with platinum electrodes for the 2.42 normal solution, the temperature coefficient for both

TABLE I. *Temperature coefficients of polarization capacity and polarization resistance for different concentrations of the electrolyte.*

Kind of Electrodes	Plain Platinum			Gold		
Concentration of Electrolyte	0.63 N	1.50 N	2.42 N	0.63 N	1.50 N	2.42 N
C_{18}	28.5	44.3	55.3	7.0	10.0	12.6
$(dC/dT)_{18}$	0.29	0.448	0.466	0.0372	0.053	0.067
$(1/C_{18})\ (dC/dT)_{18}$	0.0101	0.0101	0.0084	0.0053	0.0053	0.0053
R_{18}	4.3*	3.5	2.9	16.7	13.8	12.2
$(dR/dT)_{18}$	−0.045	−0.032	−0.026	−0.067	−0.043	−0.040
$(1/R_{18})\ (dR/dT)_{18}$	−0.0092*	−0.0089	−0.0089	−0.004	−0.0033	−0.0033

Notes: Values of capacity are in microfarads per cm² for one electrode. Values of resistance are in ohms per cm² of area for one electrode. *N* signifies normal solution (H_2SO_4 in water), i.e., 49 grams of acid per liter of solution. The frequency was constant at 1000 cycles per second.

* This value is somewhat uncertain, due to the fact that the electrodes were not fully conditioned.

Relatively, the values of C_{18} and R_{18} in Table I are accurate to within about 1 percent. Values of $(dC/dT)_{18}$ and $(dR/dT)_{18}$, and, consequently, the values of temperature coefficients, are probably not more accurate than to within 5 percent.

gold and platinum electrodes is independent of concentration for the three values of concentration involved. In other words, C_{18} and $(dC/dT)_{18}$ change in the same manner with respect to changes in concentration.

Also, it may be seen that the values of resistance per unit area of electrode, R_{18}, with platinum are about one-fourth the values for the corresponding concentrations with gold electrodes. On the other hand, values of capacity per unit area are about four times as large with platinum as with gold electrodes for corresponding concentrations. It may be noted from the curves in Fig. 4 that capacity and resistance do not vary linearly with temperature in the cases with platinum electrodes as they do with the gold electrodes.

The value of temperature coefficient of capacity as obtained in this work for platinum electrodes is somewhat less than that computed from the data given by Sheldon, Leitch and Shaw.[9] The value computed from their data is about 0.02 per degree centigrade when compared to the capacity at a temperature of 18°C.

The degree of variation of the product, capacity of cell times total resistance of cell (regarded as the polarization resistance), is shown in Table II. The corresponding values of the angle of phase difference are also shown in many instances. Although in Table II, the capacity and resistance of the cell were used rather than the values for a single electrode, nevertheless, regarding the capacity and resistance as being in series, the product would not be changed in value in considering the results for a single electrode, for in that case the value of capacity would be double the total capacity of the cell and the value of resistance would be one-half the total resistance of the cell. Since the frequency was constant, Table II also indicates the variations in the tangent of the angle of phase difference for the different conditions represented by the several curves. It may be noted that there is no large

[9] Sheldon, Leitch and Shaw, reference 1.

variation in the phase difference for any one temperature run. With gold electrodes, the phase difference seems to increase slightly with rising temperature, while with platinum electrodes, for the higher concentrations especially, the phase difference seems to be slightly lower at the higher temperatures. For both kinds of electrodes, the phase difference increases with increase in concentration of the electrolyte.

TABLE II. *Variation in product, $C \times R$, with temperature, frequency being constant.*

Kind of electrodes	Plain Platinum			Gold		
Concentration	0.63 N (H_2SO_4)	1.50 N (H_2SO_4)	2.42 N (H_2SO_4)	0.63 N (H_2SO_4)	1.50 N (H_2SO_4)	2.42 N (H_2SO_4)
	134 (40°10′)	158 (44°48′)	162 (45°34′)	113 (35°30′)	131 (39°27′)	142 (41°52′)
	137	159	163	115	133	147
	139	160	161	116	136	153
Temperature increasing	140 (41°20′)	160 (45°15′)	162	116	139	156
	140	158	159 (45°3′)	117 (36°20′)	140 (41°30′)	159
	139	157	158	118	141	161 (45°22′)
	139	156	158	118	142	160
	138	154	157	118 (36°30′)	143 (41°57′)	159 (45°2′)
Maximum temperature	138 (41°5′)	152 (43°40′)	155 (44°15′)	117	142	
	139	152	154	111?	141	167?
	141	153	157	115	141	159
Temperature decreasing	142	155	159	114 (35°43′)	140 (41°20′)	157
	143 (42°5′)	156	161 (45°27′)	114	138	155
	143	158	161	114	137	153
	141	160	163	114	135 (40°22′)	150
	139	161 (45°18′)	163	113	133	147
	137 (40°50′)	160	164 (45°51′)	114	133	145 (42°20′)
Average	139 (41°00′)	157 (44°27′)	160 (45°10′)	115 (36°00′)	138 (40°54′)	154 (44°8′)

Note: The average values of the angle of phase difference are computed from the average values of $(C \times R)$.

In Fig. 5 are curves showing the results of attempted runs after the electrodes had been polarized with oxygen or hydrogen, as indicated in the figure. The electrodes were polarized by connecting the two together and

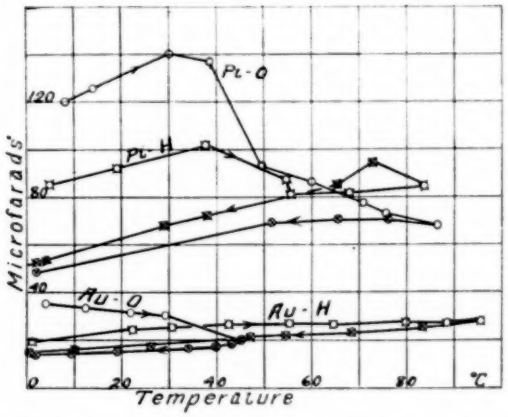

Fig. 5. Curves, capacity versus temperature, for polarized electrodes. The kind of electrodes and type of polarization are indicated in the figure. In all cases, the concentration was 1.46 N and the frequency was 1000 cycles per sec. Values of capacity are in microfarads per cm^2 for one electrode.

to the appropriate terminal of a direct current source of potential while a comparatively large third electrode was connected to the other terminal. Excepting in the case of gold polarized with oxygen, the capacity increased

regularly on starting the runs, but at temperatures of about 35° or higher there were sudden and irregular decreases in the value of capacity. Such decreases usually occurred simultaneously with the appearance of gas on the faces of the electrodes. Continuing the runs throughout the range of temperatures, the final values of capacity were much lower, yet still somewhat higher than the minimum values.

Temperature Coefficient at Different Frequencies

Curves, capacity versus temperature, representing measurements at different frequencies, but with the concentration constant, are very similar to those of Fig. 4. The slopes of the curves decrease considerably with increasing frequency. For platinum the temperature coefficient increases with increasing frequency, while the opposite seems to be true in the case with gold electrodes. The results of such tests are given in Table III. As may be seen from the table, both capacity and resistance decrease markedly with increasing frequency (see under C_{18} and R_{18}).

The variation of polarization capacity and resistance with frequency has been the subject of special investigations by Merritt,[10] Jolliffe,[11] and Wolff.[12] The results found in this work for variation of capacity with frequency, although representing a comparatively narrow and somewhat lower range of frequencies, are in general agreement with the results of their investigations.

Table III. *Temperature coefficient of capacity at different frequencies.*

Kind of Electrode	Plain Platinum				Gold	
Frequency	645.0	1290.0	2581.0	3872.0	645.0	2581.0
C_{18}	60.6	42.4	28.2	21.3	14.7	7.6
$(dC/dT)_{18}$	0.487	0.356	0.250	0.205	0.111	0.048
$(1/C_{18})\ (dC/dT)_{18}$	0.0080	0.0084	0.0088	0.0096	0.0075	0.0063
R_{18}	4.56	3.18	2.0	1.9	15.5	6.5
$(dR/dT)_{18}$	−0.034	−0.028	−0.015	−0.015	−0.083	−0.029
$(1/R_{18})\ (dR/dT)_{18}$	−0.0075	−0.0088	−0.0075	−0.0088	−0.0053	−0.0045

Notes: Values of frequency are in cycles per second. Values of capacity are in microfarads per cm² for one electrode. Resistance is in ohms per unit area of electrode. The concentration, 1.46 normal, was the same in all cases.

Discussion

It is very well known that temperature affects in a very important way most electrolytic processes. The temperature coefficient of conductivity of sulphuric acid of normal concentration as given in tables by Kohlrausch and Holborn[13] is about 0.012 per degree centigrade at a temperature of 22°C. Also, the temperature coefficient of fluidity as based on data from tables is positive with a value of about 0.028 per degree centigrade at 15°C. In consideration of the facts that the temperature coefficients of capacity for platinum and gold in sulphuric acid are not the same and that the variation of

[10] Merritt, Phys. Rev. **17**, 524 (1921).

[11] Jolliffe, Phys. Rev. **22**, 293 (1923).

[12] Wolff, reference 4.

[13] Kohlrausch and Holborn, Leitvermögen der Electrolyte (1916).

capacity with temperature is not linear in the case with platinum, while it is in the case with gold, the temperature coefficients of capacity and resistance are not fully accounted for in variations of conductivity and fluidity with temperature, for if so the coefficients for the two metals would be affected alike.

Knobel and Joy[14] found, with smooth platinum, that increasing the temperature had the effect of decreasing the overvoltage. Overpotential and catalytic activity of metals, according to the work of Rideal,[15] vary inversely, i.e., metals arranged in order of decreasing catalytic activity are also arranged in order of increasing overpotential. Bancroft,[16] also, states that the metals which have a lower overvoltage are those that catalyze the reaction, $2H \rightarrow H_2$, while those which have a high overvoltage do not. Among other things, Bancroft also discusses the action of the so-called catalytic poisons in preventing catalysis. Now Wolff[17] has shown that catalytic poisons have the effect of decreasing polarization capacity. It seems quite likely, therefore, that overvoltage, catalytic activity, and polarization capacity are related in an important and probably a very complex way. The decrease in capacity of the electrode as it acquires its stable condition after polishing would mean a corresponding decrease in its catalytic activity. The increase in capacity with temperature would mean an increase in catalytic activity and a reduction in the conditions favorable to overvoltage, as found by Knobel and Joy. It is recognized that in considering polarization capacity in relation to overvoltage one is dealing with much lower values of voltage in the case of polarization capacity, and for so-called minimum capacity, values of voltage which are thought to be strictly reversible.

If polarization capacity and catalytic activity are intimately related, then the results of this paper do not seem to be in full agreement with the work of Bowden and Rideal[18] who found that the specific catalytic activity of the various metals, including platinum, for the electro-deposition of hydrogen suffer only small variations by thermal treatment. Here again, however, the full conditions are not the same, for in this work the capacity was determined by means of a bridge supplied with alternating current and, consequently, not only is the deposition of hydrogen involved, but also the deposition of oxygen and the effect of one on the other after consecutive reversals of the current.

In conclusion, the writer desires to express appreciation of the excellent facilities available at Cornell University, Department of Physics, for doing this work. Thanks are extended to Professor E. Merritt, who approved this problem and under whose direction the work was done, for his interest and many helpful suggestions. The writer is also indebted to Professor C. C. Murdock for his interest in the results of the work and a discussion of their relation to other problems of polarization capacity.

[14] Knobel and Joy, Trans. Am. Electrochem. Soc. **44**, 443 (1923).

[15] Rideal, Jour. Am. Chem. Soc. **42**, 94 (1920).

[16] Bancroft, Trans. Am. Electrochem. Soc. **37**, 21 (1920).

[17] Wolff, unpublished paper.

[18] Bowden and Rideal, Proc. Royal Soc. of London **A120**, 80 (1928).

ON THE SOLUTION OF CERTAIN CASES OF THE GENERAL EQUATION OF DIFFUSION

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(Received January 13, 1930)

Abstract

For diffusion in substances for which the conductivity and diffusivity are functions of temperature, the partial differential equation which determines the temperature is non-linear in character. For a certain class of boundary conditions the introduction of an auxiliary function of time and distance reduces this equation to an ordinary differential equation of the second order, in which the temperature and the auxiliary function appear as dependent and independent variables respectively. As this resulting equation can be solved by methods of approximation, the solution to the original equation can be thus obtained.

The conditions under which such an auxiliary function exists are examined and a simple criterion developed by means of which it may be determined whether such a function exists for any particular case. The method is shown to apply to the case of the semi-infinite solid, and the solution of a particular problem of this type (the cooling of a steel ingot) is given. Another case to which the method applies (diffusion in an axially heated cylinder) is considered, and shown to afford a possible method for determining diffusivity as a function of temperature. It is noted that the method developed is available for the solution of problems in the diffusion of matter as well as of those concerned with the diffusion of heat.

THE theory of the diffusion of heat rests upon the assumption that the quantity δQ of heat passing through a plane of area $\delta y\ \delta z$ in time δt is given by the relation:

$$\frac{\delta Q}{\delta t} = -k\frac{\partial \theta}{\partial x}\delta y\,\delta z, \tag{1}$$

where $\partial\theta/\partial x$ is the temperature gradient in the direction of the X-axis, and k is the thermal conductivity. When k is taken as a constant, this assumption leads to the well-known differential equation,

$$\frac{\partial \theta}{\partial t} = h^2\left(\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}+\frac{\partial^2\theta}{\partial z^2}\right), \tag{2}$$

in which the diffusivity h^2 is the ratio k/cd, c being the specific heat and d the density. If h^2 is taken as a constant, Eq. (2) may be solved for many particular cases by well-known methods.

If k is not a constant, but a function of θ, Eq. (2) no longer applies. The differential equations that then apply for linear and radial flow have been given by many authors; and the general form is easily obtained in a manner analogous to the usual derivation of Eq. (2). The flow into and out of a differential block through the two faces normal to the direction of the X-axis is evidently, from Eq. (1), given by

$$\frac{\delta Q}{\delta T}_{(x)} = -\left(k-\frac{1}{2}\frac{\partial k}{\partial x}\delta x\right)\frac{\partial}{\partial x}\left(\theta-\frac{1}{2}\frac{\partial \theta}{\partial x}\delta x\right)\delta y\,\delta z$$
$$+\left(k+\frac{1}{2}\frac{\partial k}{\partial x}\delta x\right)\frac{\partial}{\partial x}\left(\theta+\frac{1}{2}\frac{\partial \theta}{\partial x}\delta x\right)\delta y\,\delta z$$
$$=\left(k\frac{\partial^2\theta}{\partial x^2}+\frac{\partial k}{\partial x}\frac{\partial \theta}{\partial x}\right)\delta x\,\delta y\,\delta z.$$

Similar equations apply to the flow into and out of the other two pairs of faces, and the total increment of heat in the differential block is given by the addition of the increments through the three pairs of faces. As the temperature θ is defined by Q/cd. $\delta x\,\delta y\,\delta z$, and if k is a function of θ only, there is finally obtained:

$$f(\theta)\frac{\partial \theta}{\partial t}=\left(\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}+\frac{\partial^2\theta}{\partial z^2}\right)+\frac{1}{k}\frac{dk}{d\theta}\left\{\left(\frac{\partial \theta}{\partial x}\right)^2+\left(\frac{\partial \theta}{\partial y}\right)^2+\left(\frac{\partial \theta}{\partial z}\right)^2\right\}, \qquad (3)$$

where $f(\theta)$ is written for $1/h^2$ or cd/k, as c and d may also be functions of θ. Eq. (3) is the general form of the equation for heat conduction, and reduces to Eq. (2) for the special case where k and h^2 are constants. As is well known, the same equations apply to the diffusion of gases and liquids when θ represents the concentration, k the diffusion constant, and cd the concentration-pressure ratio. The material presented below applies therefore to problems in the diffusion of matter as well as to those dealing with the diffusion of heat.

Due to its non-linear character, Eq. (3) cannot be solved by the methods applicable to Eq. (2). In papers[1] dealing with the experimental determination of k and h^2 will be found discussions of Eq. (3), usually for the case of linear flow $[\partial\theta/\partial y=\partial\theta/\partial z=0]$. The usual treatment is to employ the solutions of Eq. (2) with approximate corrections applicable to the particular problem. This procedure is facilitated by the use of formal solutions to Eq. (3) such as those obtained by Glage[1] and by Kirchhoff and Hansemann,[2] among others.

Problems in the interdiffusion of gases have been similarly treated. Boltzmann[3] in particular developed formal solutions to Eq. (3) applicable to a number of cases. In the case of the semi-infinite solid, he showed that the solution to Eq. (3) could be expressed formally in terms of the quantity x^2/t only. Advantage has been taken of this relation in the treatment of special cases by Wiedeburg[4] and Germond.[5] The procedure given below for the solution of the semi-infinite solid rests upon this same fact: the method will be first discussed in more general terms.

[1] Glage, Ann. d. Physik (4) **18,** 904 (1905). This paper gives a critical resume of the classical work in this field.

[2] Kirchhoff and Hansemann, Wied. Ann. **9,** 1 (1880).

[3] Boltzmann, Wien. Ber. **86,** 63 (1882); Ann. d. Physik **53,** 959 (1894).

[4] Wiedeburg, Ann. d. Physik **41,** 675 (1890).

[5] Germond, Bull. Am. Math. Soc. **35,** 460 (1929).

II. The discussion will be limited to the solution of Eq. (3) subject to boundary conditions of the type

$$\theta = c_1 \quad \text{when} \quad F_1(x, y, z, t) = 0. \qquad (4)$$
$$\theta = c_2 \quad \text{when} \quad F_2(x, y, z, t) = 0.$$

If θ is so defined, it may be proved that if there exists a function $\Phi\ (x, y, z, t)$ meeting the following conditions:

$$\Phi = C_1 \quad \text{when} \quad F_1(x, y, z, t) = 0,$$
$$\Phi = C_2 \quad \text{when} \quad F_2(x, y, z, t) = 0, \qquad (5)$$

$$\frac{\partial \Phi}{\partial t} = \frac{\left(\frac{\partial \Phi}{\partial x}\right)^2 + \left(\frac{\partial \Phi}{\partial y}\right)^2 + \left(\frac{\partial \Phi}{\partial z}\right)^2}{f_1(\Phi)} = \frac{\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2}}{f_2(\Phi)}, \qquad (6)$$

where $f_1(\Phi)$ and $f_2(\Phi)$ are functions of Φ only, then θ is a function of Φ only, and,

$$(f(\theta) - f_2(\Phi))\frac{d\theta}{d\Phi} - f_1(\Phi)\frac{d(\log k)}{d\theta}\left(\frac{d\theta}{d\Phi}\right)^2 = f_1(\Phi)\frac{d^2\theta}{d\Phi^2}. \qquad (7)$$

For the function θ obtained by integration of Eq. (7) subject to the boundary conditions, $\theta = c_1$ when $\Phi = C_1$, $\theta = c_2$ when $\Phi = C_2$, satisfies Eqs. (4) and also Eq. (3), as the latter, when θ is taken as a function of Φ, reduces to Eq. (7) by virtue of Eqs. (6). Hence θ is the required solution, and the theorem is proved.

In what follows, a function satisfying Eqs. (6) for particular boundary conditions of the type of Eqs. (5) will be termed a resolving function for those boundary conditions.

III. Suppose now that a function θ' has been determined in the above manner for a case of Eq. (3) in which $f(\theta')$ is any function whatever of θ' but in which k is a constant, and the second term to the right of Eq. (3) is therefore zero. Then,

$$\frac{\partial \theta'}{\partial t} = \frac{\frac{\partial^2 \theta'}{\partial x^2} + \frac{\partial^2 \theta'}{\partial y^2} + \frac{\partial^2 \theta'}{\partial z^2}}{f(\theta')}.$$

This is formally identical with the second of Eqs. (6). Substitution for Φ in terms of θ in the first of Eqs. (6) yields:

$$\frac{\partial \theta'}{\partial t} = \frac{\left(\left(\frac{\partial \theta'}{\partial x}\right)^2 + \left(\frac{\partial \theta'}{\partial y}\right)^2 + \left(\frac{\partial \theta'}{\partial z}\right)^2\right)\frac{d\Phi}{d\theta'}}{f_1(\Phi)}.$$

But as Φ is a function of θ' only, $f_1(\Phi)/(d\Phi/d\theta')$ is a function of θ' only. Hence this equation is formally identical with the first of Eqs. (6). There-

fore θ' is itself a resolving function for the particular boundary conditions involved.

It follows that if any resolving function exists for particular boundary conditions, then any solution of Eq. (3) (i.e., θ') when k is constant is, whatever the form of $f(\theta')$, itself a resolving function for these particular boundary conditions.

Applying this theorem to the special case $f(\theta')=1$, it follows that if any resolving function exists, the solution to this special case is itself a resolving function. But the solutions to this special case are precisely the well-known solutions to Eq. (2) ($h^2=1$). Such solutions satisfy the second of Eqs. (6); it is a simple matter to determine by numerical trial if they satisfy the first of these equations. If they do, values of $f_1(\theta')$ vs. θ' may be computed, $f_2(\theta')=1$, and a solution to Eq. (3) may be obtained by integration of Eq. (7). If they do not, it is proved that no resolving function exists, and the method fails.

The criteria for the use of the method are then that the boundary conditions be of the form of Eqs. (4) and that the known solution θ' for the case $k=$ constant, $f(\theta')=1$ satisfies both of Eqs. (6).

IV. By actual trial it has been found (in the manner described above) that the method is not applicable to many important cases, such as the diffusion in a slab or cylinder of infinite length when the temperature at the surface is kept constant. It is, however, applicable to the important case of the semi-infinite solid. If in such a solid the initial temperature is θ_0, while the temperature at the surface $x=0$ is always θ_1, then Eq. (3) becomes:

$$f(\theta)\frac{\partial\theta}{\partial t}=\frac{\partial^2\theta}{\partial x^2}+\frac{d(\log k)}{d\theta}\left(\frac{\partial\theta}{\partial x}\right)^2. \tag{8}$$

The problem is then to solve Eq. (8) subject to the conditions,

$$\begin{aligned}\theta&=\theta_0 \quad \text{when} \quad t=0,\\ \theta&=\theta_1 \quad \text{when} \quad x=0.\end{aligned} \tag{9}$$

For this problem a resolving function is given by,

$$\Phi=e^{-x/t^{1/2}}. \tag{10}$$

Then from Eqs. (6) and (7), θ is given by integration of

$$\left(\frac{f(\theta)\log\Phi}{2}+1\right)\frac{d\theta}{d\Phi}+\Phi\frac{d(\log k)}{d\theta}\left(\frac{d\theta}{d\Phi}\right)^2+\Phi\frac{d^2\theta}{d\Phi^2}=0, \tag{11}$$

subject to the conditions,

$$\begin{aligned}\theta&=\theta_0 \quad \text{when} \quad \Phi=0,\\ \theta&=\theta_1 \quad \text{when} \quad \Phi=1.\end{aligned} \tag{12}$$

This integration may be accomplished for any particular case by any of the well-known methods of successive approximations.

This result is of some importance in the solution of physical problems. The most common type of problem in the diffusion of heat involves an initial constant temperature and thereafter the maintenance of another constant temperature on some surface. For all such cases the result for the semi-infinite solid serves as a first approximation, applicable within a high degree of accuracy for an initial time interval sufficiently small. Thus for diffusion in a slab, cylinder, or sphere, the temperature will vary with time and distance from the surface in the same way as for the semi-infinite solid from zero time up to that which the temperature at the center varies by more than the required order of accuracy from its initial value, with the further proviso for the sphere and cylinder that the portion in which the temperature maintains substantially its initial value extend out to a radius beyond which the curvature may be neglected with sufficient accuracy.

V. As an actual example of the method discussed in the preceding section there will be considered the case of the cooling of a large steel ingot, a problem for which the simpler case is discussed by Ingersoll and Zobel, p. 85.[6] Strictly comparable values of the relations between diffusivity and temperature and between conductivity and temperature were not found in the literature, but data were taken from the Landolt-Börnstein Tables which were thought to be sufficiently representative of a low carbon steel. The diffusivity was taken as that given for Bessemer steel from the data of Kirchhoff and Hansemann,[7] giving the diffusivity as: $1/f(\theta)=h^2(1+\beta\theta)$, where $h^2=0.1148$ and $\beta=-0.00019$. The conductivity was taken from the mean values given in the Tables[8] for a 0.64 percent carbon steel, which gave, for the usual approximation of a linear relation: $k=k_0(1+\alpha\theta)$, where $k_0=0.115$ and $\alpha=-0.00046$.

Thus, from Eqs. (11) and (12), the temperature in the block is given by ntegration of:

$$\frac{d^2\theta}{d\Phi^2}=-\left(\frac{\log\Phi}{2h^2(1+\beta\theta)}+1\right)\frac{1}{\Phi}\frac{d\theta}{d\Phi}-\frac{\alpha}{1+\alpha\theta}\left(\frac{d\theta}{d\Phi}\right)^2, \tag{13}$$

subject to the boundary conditions which were that $\theta=800$ when $\Phi=0(t=0)$, and $\theta=20$ when $\Phi=1(x=0)$.

The method of solution employed was that of successive approximations in which the integrations are mechanically obtained by means of an integraph, as described in a paper by Fry.[9] The work was simplified by taking as a first approximation the well known solution to the problem when h^2 and k are constant, which may be written in terms of Φ as

$$\theta=800-\frac{2\times780}{\pi^{1/2}}\int_{-(\log\Phi/2h)}^{\infty}e^{-\lambda^2}d\lambda. \tag{14}$$

In this expression h was taken as having its mean value for the temperature range involved or $(0.1060)^{1/2}$. Due to the discontinuity at $\Phi=0$ and

[6] Ingersoll and Zobel, Mathematical Theory of Heat Conduction.

[7] Kirchhoff and Hansemann, Wied. Ann. **13**, p. 406 (1881).

[8] Landolt-Börnstein Tabellen, 5th Ed. p. 1291 (1923).

[9] T. C. Fry, Proc. Int. Math. Congress, Vol. II, p. 405, Toronto (1924).

various associated peculiarities of the equation, some slight modifications in procedure were necessary. Each approximation was made as follows: Given approximations for θ and its first derivative, say θ_n and θ_n' respectively, the corresponding second derivative θ_n'' was computed from Eq. (13). This was then integrated to give θ'_{n+1}, the constant of integration being taken such as to give θ'_{n+1} the same value at $\Phi=1$ as that found at this point for θ_n'. In general, this did not make θ'_{n+1} approach zero as Φ approaches zero, a condition which must be satisfied, as is evident from the fact that a function of the type of Eq. (14) is a close approximation to a solution for low values of Φ. Hence θ'_{n+1} was corrected to meet this requirement by taking values of θ proportional to the second term of Eq. (14) up to such a value of Φ as would make this approximation merge into the original curve for θ'_{n+1} without any abrupt change in curvature. The θ'_{n+1} thus corrected

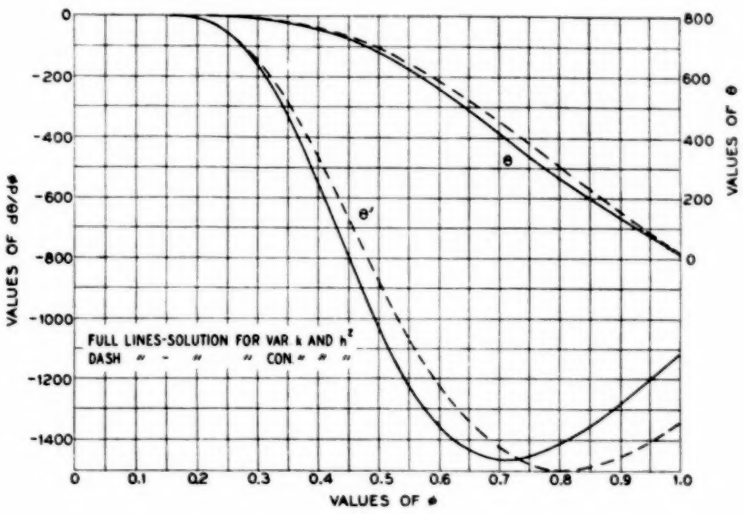

Fig. 1.

was integrated to give θ_{n+1}, the constant of integration being such as to make $\theta_{n+1}=800$ at $\Phi=0$. The difference between 20 and the value of θ_{n+1} at $\Phi=1$, or C, was taken as a correction factor, and a term ΦC added to θ_{n+1} to make it meet both boundary conditions, while the term C was also added to θ'_{n+1}, in accordance with the procedure developed by Fry.[9] Then θ'_{n+1} was again corrected to make it approach zero as Φ approached zero, by the same method as described above. The values of θ_{n+1} and θ'_{n+1}, thus finally obtained were used to compute θ''_{n+1} and the operation repeated until successive approximations produced no change in θ or θ'.

The solution obtained for the case cited is shown graphically in Fig. 1, in which both θ and θ' are given. The corresponding solution and its first derivative for the case in which the conducitivity and diffusivity are constant (the latter taken as $h^2=0.1060$), as given by Eq. (14), are shown in broken lines. It will be seen that the solutions to the two cases differ con-

siderably. To emphasize this difference, Fig. 2 has been prepared, corresponding to Fig. 12, p. 86 of Ingersoll and Zobel,[6] and giving the rate of cooling $(\partial\theta/\partial t)$ at distances of 0.3 cm and 1.0 cm from the face of the block. The broken lines again show the corresponding curves for constant diffusivity and conductivity. It is apparent that consideration of the variation in the conductivity and diffusivity results in a higher maximum rate of cooling than if this variation is neglected.

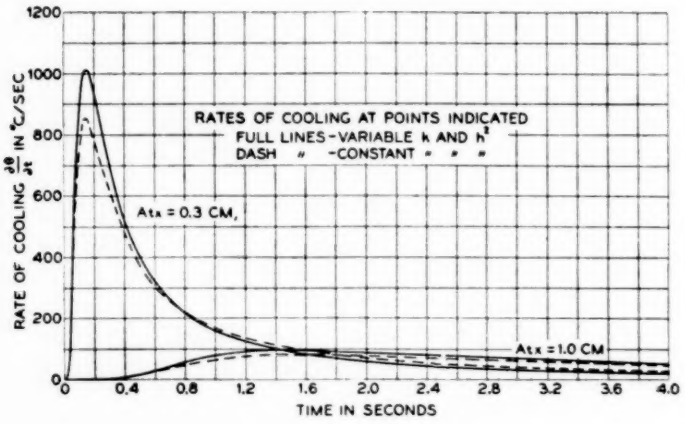

Fig. 2.

VI. Another case in which the method applies is that of a cylinder of infinite length and radius, initially at one constant temperature, of which the axis is thereafter kept at another constant temperature. If x is the radial distance of any point from the axis, the problem is to solve:

$$f(\theta)\frac{\partial\theta}{\partial t}=\frac{1}{x}\frac{\partial\theta}{\partial x}+\frac{\partial^2\theta}{\partial x^2}+\frac{d(\log k)}{d\theta}\left(\frac{d\theta}{dx}\right)^2, \tag{15}$$

subject to the conditions,

$$\begin{aligned}\theta&=\theta_0 \quad \text{when} \quad t=0,\\ \theta&=\theta_1 \quad \text{when} \quad x=0.\end{aligned} \tag{16}$$

For this case also the Φ of Eq. (10) is a resolving function. From Eqs. (6) and (7), θ is given by integration of

$$\left(\frac{f(\theta)\log\Phi}{2}+\frac{1}{\log\Phi}+1\right)\frac{d\theta}{d\Phi}+\Phi\frac{d(\log k)}{d\theta}\left(\frac{\partial\theta}{\partial\Phi}\right)^2+\Phi\frac{d^2\theta}{d\Phi^2}=0. \tag{17}$$

subject to the conditions of Eqs. (12).

Brown and Furnas[10] have discussed the determination of a variable diffusivity by the graphical integration of Eq. (15) for numerical values of the differential terms of this equation in the case of a centrally heated cylinder.

[10] Brown and Furnas, Trans. Am. Inst. Chem. Engineers **18**, 295 (1926).

The above development suggests a procedure in which the measurements and computation would be simpler, though the experimental conditions would be more difficult to obtain, as to maintain a constant temperature along the axis would require some method of adjusting the current in the central heating coil in such a way as to fulfill this condition. It would also be necessary to limit the measurements to a temperature range such that the surface never varied appreciably from its initial value. If these conditions are fulfilled Eq. (17) applies, and (assuming k known as a function of θ^*), it is only necessary to take readings from one thermocouple (one value of x), as θ is a function of Φ only, and any value of Φ will be obtained at any x for some value of t. Expressing the values of t in terms of Φ, values of θ vs. Φ are experimentally obtained. Then by graphical differentiation, or numerically by successive differences, values of $d\theta/d\Phi$ and $d^2\theta/d\Phi^2$ may be obtained, and Eq. (17) solved for $f(\theta)$, the reciprocal diffusivity, as a function of temperature.

VII. The development discussed above permits the reduction of the general differential equation of diffusion to a single ordinary differential equation of the second order, which can be readily solved by methods of approximation. The only particular case of major importance to which the method applies is that of the semi-infinite solid, which affords, however, a good approximation to a solution for many other cases within limited ranges of the co-ordinates of time and distance. The form of the differential equation resulting when the method applies is such as to make the solution by the method of successive approximations preferable, and for this graphical methods are more convenient than numerical.

As is apparent in the example given above, solutions obtained by this method when the variations in conductivity and diffusivity are allowed for may differ considerably from those obtained on the assumption that these quantities are constant. Such differences may be particularly apparent in the values obtained for rates of cooling or of temperature gradients, as the example again indicates, and it is in the evaluation of these quantities that most accurate determinations are desirable (*e.g.*, in the casting of metals and glass). It must, however, be admitted that conditions in technical operations seldom approach those of the mathematically ideal problem sufficiently to make such accuracy in calculation significant, and the developments discussed above are more likely to be of practical importance in problems concerned with material diffusion than in those involving heat.

Acknowledgment is due Dr. T. C. Fry of these Laboratories for much helpful criticism of the work reported in this paper.

* This relation would be previously determined by measurements for the steady state, as discussed by Brown and Furnas (reference 10).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

On the Theory of Electrons and Protons

In a recent paper,[1] Dirac has suggested that the reason why the transitions of an electron to states of negative energy, which are predicted by his theory of the electron, do not in fact occur is that nearly all of the states of negative energy are already occupied. Dirac has further shown that the unoccupied states of negative energy have many of the properties of protons; that, for instance, they may be represented by wave functions which would be taken to correspond to a particle of positive charge and positive mass. He has further shown that the mass associated with these gaps is not necessarily the same as that of the electron, and he has suggested the assumption that the gaps are protons. In order to account for the fact that the divergence of the electric field is not, in spite of the infinite electron density, everywhere infinite, Dirac further assumes that only the departures from the normal state in which all negative states are filled are to be counted in computing the charge density for Maxwell's fourth equation

$$\text{div } E = -4\pi\rho. \qquad (1)$$

Finally, Dirac is able to account for the validity of the Thomson formula for the scattering of soft light by a free electron, in spite of the fact that the derivation of this formula on his theory of the electron—a derivation which makes explicit use of the transitions to states of negative energy which are now forbidden, is invalid. According to Dirac, the scattering takes place by a double electron jump, in which a negative[2] electron jumps up to some state of positive energy, and the original positive electron falls down into the gap left.

There are several grave difficulties which arise when one tries to maintain the suggestion that the protons are the gaps of negative energy, and that there are no distinctive particles of positive charge. In the first place, we can easily see that Dirac's theory requires an infinite density of positive electricity; and since we should expect the de Broglie waves of this charge to be quantized, we should expect some corpuscular properties for the positive charges. The reason why the theory requires an infinite positive charge is this: If the explanation of the scattering of an electron is to be tenable, a negative electron must interact with the electromagnetic field in the way predicted by Dirac's theory of the electron; for otherwise the scheme proposed would not give the Thomson formula. But this means that there must be a term involving the current and charge vector of the negative electrons in the total energy momentum tensor for matter and radiation. Thus by (1), the divergence of the electric field will be everywhere infinite unless there is an infinite density of positive electricity to compensate the negative electrons.

A further difficulty appears when we try to compute the scattering of soft light by a proton. This difficulty is not unconnected with the difference in mass between the electron and proton, and makes it seem improbable that this difference can be explained on the basis suggested by Dirac. For the scattering process must in this case be regarded as a double jump of a single electron, in which a negative electron jumps to some state of positive energy, and then falls back into the hole that is the original proton. Now it is easy to see that the probability of this

[1] P. Dirac, Roy. Soc. Proc. **A126**, 360 (1930).

[2] By a negative electron we mean an electron of negative energy.

scattering is determined by precisely the same matrix components as those which give the electron scattering, and that the present theory gives equal scattering coefficients for electron and proton. Of course, the interaction between electrons is omitted in this computation; but the difficulty is this, that such interaction would affect electron scattering and proton scattering in precisely the same way; whereas the Thomson formula requires the latter to be smaller by a factor proportional to the square of the ratio of the masses.

Finally, there is a numerical discrepancy to be noted. According to Dirac's suggestions, the filling of the proton gaps in the distribution of negative electrons should correspond to the annihilation of an electron and a proton, and should thus, under all normal conditions, be a very rare occurrence. Now if we consider for definiteness a free electron in an enclosure in which there are n_p free protons per unit volume, we may readily compute the rate at which the electron should, by the Dirac radiation theory, fall into one of the corresponding gaps. The conservation laws require that at least two quanta be emitted in this process; and it is sufficient to consider jumps in which no more than two quanta are emitted. The details of the calculation will be published elsewhere; if we neglect the interaction of the electron with the negative electrons we obtain for the mean life time of the electron:

$$T = Gm^2c^3e^{-4}/n_p \qquad (2)$$

where G is a numerical constant of the order of unity, e the charge, and m the mass of the electron. Now again it is difficult to see what large errors could be involved in the computation, since the matrix components which give (2) are of precisely the same type as those which give correctly the Thomson formula and the optical transition probabilities of the electron; and (2) gives a mean life time for ordinary matter of the order of 10^{-10} seconds.

Thus we should hardly expect any states of negative energy to remain empty. If we return to the assumption of two independent elementary particles, of opposite charge and dissimilar mass, we can resolve all the difficulties raised in this note, and retain the hypothesis that the reason why no transitions to states of negative energy occur, either for electrons or protons, is that all such states are filled. In this way, we may accept Dirac's reconciliation of the absence of these transitions with the validity of the scattering formulae.

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February 14, 1930.

The Collision Diameter of the Hydrogen Atom

Harteck measured the viscosity of monatomic hydrogen and calculated the collision radius to be $r_H = 1.3 \times 10^{-8}$ cm (r_0 of the first Bohr orbit is 0.53×10^{-8} cm). We have measured the decrease of intensity of a fine beam of monatomic hydrogen in passing through 3.0 cm of mercury vapor at 0.000185 mm Hg and find the decrease of intensity to be 23 percent. If the collisions are supposed to be between elastic spheres the sum of their radii is 6.2×10^{-8} or assuming $r_{Hg} = 1.8 \times 10^{-8}$, the radius of hydrogen atom is 4.4×10^{-8}. This is larger than would be assumed even on wave mechanics unless there is very considerable resonance interaction between mercury and hydrogen.

E. G. LUNN
F. R. BICHOWSKY

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February 17, 1930.

Excited Radicals in Chemical Compounds

The letter of Mr. D. H. Andrews in your number of December 15th makes the important point it is possible to assign definite frequencies to vibrating groups in the molecule, and that these frequencies are constant, to a first approximation, from molecule to molecule e.g. the value of the vibration frequency of C–H in any molecule will be of the order of 3000 cm^{-1}, altering only slightly with change of environment. Although some of Mr. Andrews' values are open to question, there is a weight of evidence, both from the Raman effect and from infra-red spectra, for the essential correctness of his statement;

the failure to realise it has been the cause of false analyses of the spectra of several polyatomic molecules, in which the frequency of, say, the CO group has been given values varing from 1500 to 200 cm^{-1}.

It is possible, however, to go much further. First, the frequency of a group, which remaining constant in molecules where the chemical environment is the same, can undergo a sharp change to a second value corresponding to a second chemical environment. I was led to this conception from a study of the building-up of the N_2O molecule from NO. The analysis of the vibration-rotation band system of N_2O (to be published shortly) shows that the molecule is linear and symmetrical. The vibration of N–O along the axis of the molecule is 2250 cm^{-1}. Now the frequency of the NO molecule in its normal ($^2\Pi$) state is 1892 cm^{-1}; the building of the N_2O molecule has brought about a very definite change. A name can be given to this change when it is realized that the frequency of the first excited ($^2\Sigma$) state of NO is 2345 cm^{-1}. The numerical resemblance is striking; and it becomes more than a coincidence when we find that the only other excited state ($^2\Pi$) so far known has a frequency of 1030 cm^{-1}, and that the Raman effect and infra-red spectra of compounds containing the NO group give a value *c.* 1000 without exception. With these frequencies it is possible to fit all the results upon the NO group at present known i.e. a diatomic group within a polyatomic molecule can be described in terms of the excited states of a diatomic molecule.

The results are even more definite when the CO group is considered. In a normal ketone or acid the vibration frequency is *c.* 1600 cm^{-1}. The Raman evidence is contradictory but the infra-red quite convincing. On the other hand, an α-diketone of the form

R.C O
|
R.C O

seems, from the careful analysis of the absorption spectra of several compounds of this type by Louis Light of Zürich, to be of the order of 1100 cm^{-1}.

The first three states of the CO molecule are:

x	$^1\Sigma$	2155
a	$^3\Pi$?	1724
d	$^3\Sigma$?	1105

the agreement is satisfactory. The effect of the conjugated system is particularly interesting.

Certain principles may be set down, even at this early stage:

(i) A diatomic group persists throughout a large number of molecules with the same vibration frequency. As Mr. Andrews suggests, this establishes the identity of covalent bindings. The mass of the atoms to which the diatomic groups are attached is of small importance.

(ii) A diatomic group can have several sharply distinct frequencies. Each of these frequencies behaves as defined in (i).

(iii) The frequencies of a diatomic group correspond to the frequencies of excited states of the appropriate diatomic molecule. A frequency corresponding to the frequency of the normal state of the molecule is not usually observed.

At the moment the attempt to put a spectroscopic name to chemical binding must stop with groups bound by covalencies. Clearly the extension of the idea to such problems as the boron hydrides is practicable; if in the B_2H_6 molecule there are B–H groups bound by singlet linkages, then the frequencies of these groups should not coincide with the frequency of any of the states of the ordinary BH molecule bound by a covalency.

Similarly, the kind of linkage shown to exist by Lennard Jones for the normal ($^3\Sigma$) state of the oxygen molecule should be responsible for abnormalities in the way outlined above. There are indications that the C–C binding in C_2H_2 is such a case; if that is true, it will be possible to indulge in a spectroscopic re-naming of the "triple" bond.

C. P. SNOW

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January 27, 1930.

The Glancing Angle of Reflection from Calcite for Silver ($K\alpha_1$) X-rays

We have measured the first order glancing angle at which the $K\alpha_1$ line of silver is reflected from the cleavage planes of calcite by a method independent of any used by those who have obtained the most reliable results so far. The weighted mean value of

fourteen independent observations reduced to 18°C is 5°17′13″.81 ±0.″06.

This value was obtained from spectrograms taken on a new spectrometer specially designed to utilize the displacement method introduced by H. S. Uhler (Phys. Rev. [2] **11,** 1–20 (1918)). A full description of the method, instrument and results will be given later.

The value of the wave-length corresponding to the above glancing angle is 0.558238A ± 0.000002A, obtained by using 3.02904A for the "effective" grating space of calcite (Siegbahn; Spectroscopy of X-Rays, 1924 Edition).

The thermal coefficient of expansion at 18°C for the grating space of calcite obtained from the most reliable sources, without approximations, is 0.0000102_3/°C. This value differs by about 2% from the generally quoted value originally given by W. Stenström (Dissertation, Lund, 1919) as a sufficient approximation.

It is interesting to note that our value of the glancing angle is 1″.4 smaller than that given by G. Kellström (Zeits. f. Physik **41,** 516 (1927)) for the first order of calcite, viz. 5°17′15″.2. The probable error of the unweighted mean of Kellström's seven determinations for this order is $\pm 0.''04_5$. The unweighted mean of his four second order determinations is also larger than ours and has relatively four times this probable error. With such a difference existing one wonders if the grating spaces of the crystal specimens used were the same. We employed an unusually selective piece of calcite which was cleaved from an excellent specimen of Iceland spar contained in the Marsh collection of Yale University.

Our value is larger than those of K. Lang (Ann. d. Physik **75,** 489 (1924)), A Leide (Dissertation, Lund (1925) and A. P. Weber (Zeits. f. Wiss. Photo. **23,** 149 (1925)) although coming within 0″.11 of Lang's and 0″.36 of Leide's results when their probable errors are added to their respective mean values.

CHARLTON DOWS COOKSEY
DONALD COOKSEY

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February 11, 1930.

BOOK REVIEWS

Quantum Mechanics. E. U. CONDON AND P. M. MORSE. Pp. 250+xiii, figs. 28. International Series in Physics, McGraw-Hill Book Co., New York, 1929. Price $3.00.

This is the first book of American authorship on the new science of quantum mechanics and should find a host of readers both here and abroad. It meets the widely felt need for an introductory text making no pretense at completeness, but aiming through numerous illustrative applications and exercises to give the reader a working knowledge of the methods of the quantum theory of today. The authors have kept the work, to use their own words, "on as elementary a plane as possible," but they have not descended to sloppy procedure in their anxiety to make easy reading.

The subject is approached from the standpoint of the statistical interpretation of the Schrödinger theory and the first three quarters of the volume is devoted to an exposition of results obtainable from the Schrödinger wave equation with a minimum of mathematical machinery. A subsequent chapter, however, gives a well written introductory account of the general formulation of the theory by Jordan, Dirac, and von Neuman, which should be helpful to many who have had difficulty in digesting the original papers on this subject.

The rather extensive treatment of diatomic molecules will be most useful to workers in the field of band spectra as there is at present no comprehensive work on the quantum mechanics of molecules. Much of the material in this chapter is derived from the valuable researches of the authors. The reviewer notes with especial pleasure the inclusion of a simplified account of the basic molecular perturbation theory of Born and Oppenheimer worked out directly for the important diatomic case.

The book also contains an interesting chapter on aperiodic phenomena.

The authors lay little emphasis on the philosophical aspect of the quantum mechanics and ignore almost completely many important phases of the subject such as the "electron spin" and the problem of dispersion. These omissions are to be reckoned a virtue rather than a drawback, however, since they enable the authors to deal with the fundamentals of the subject in a leisurely way which will be welcome to the beginner.

EDWIN C. KEMBLE

Outlines of Biochemistry. R. A. GORTNER. Pp. xv and 793. New York, Wiley and Sons; London, Chapman and Hall; 1929. Price $6.00.

Treatises in biochemistry are the successors of medical textbooks of physiological chemistry; these dealt almost exclusively with mammalian metabolism, foods, enzymes, excreta and the blood; and although when vitamins were recognized and the part played by the secretions of the endocrine glands, these matters were included, the chemistry of the life processes of plants was always beyond their scope. Even with such restrictions on the subject matter, the "conservation of energy" was referred to when dealing with the measurement of animal heat, a formula or two of chemical kinetics got in to ornament the chapter on digestion, and mention was made of the freezing-points of serums and of urine; but—with an eye, no doubt, to the limitations of the medical student—such topics received in general but incidental mention.

It is a far cry from such a book to Professor Gortner's "Outlines." He has a section on the proteins of course, including chapters on the amino-acids and the polypeptides, an up-to-date account of the vitamins written by Professor L. S. Palmer, chapters on the carbohydrates and the fats and oils, and others on the tannins and on the colouring matters of plants; but the first 290 pages of his book are devoted to "The colloidal state of matter." Here the preparation and characteristic properties of colloids are described, their electro-kinetic behaviour, and their behaviour with electrolytes and among themselves; there is a chapter on gels, and one each on hydrogen-ion-concentration, surface-tension, osmotic-pressure, and "the Donnan equilibrium."

It is obvious that in this book the generalizations of physical chemistry are not slipped in as "explanations" of an isolated fact or two, but have the place of honour; in their light the facts of physiology are examined—not mammalian alone, for as might be expected from a professor of agricultural biochemistry the plant receives its due.

To readers of The Physical Review the illustrations here afforded of the scope and power of generalizations long familiar should prove intensely interesting. Who that measures vapour-tensions will not enjoy the picture of the cactus on the wall in desert Arizona ten months without rain and sheltered from the dew, or the story of the three-months sojourn of another cactus over sulphuric acid, the account of drought-resisting cereals in Utah, winter-hardy wheat, and the drying-up of earthworms, or the human-interest paragraphs on the granary-weevils' life without a drink, the new oedema diagnosis, and the rigor of our bodies after death? All these and more are brought into the chapter on Gels to illustrate "imbibition" and the distinction between "bound" and "liquid" water; and not as incidental illustrations merely, for they are examined in the light of tables, formulas and charts, and correlated with freezing-points, osmotic-pressures and absorption in the infra-red. Therefore, if any Reader thinks he knows more physics though less biology than Gortner, let him go to it; the door is opened wide.

The sample given above could easily be matched; literature citations show where synoptic papers can be found; it would be a shame to let mere biochemists monopolize the reading of this book.

W. LASH MILLER

Introduction to Physical Optics. JOHN KELLOCK ROBERTSON. Pp. 422, figs 222. D. Van Nostrand Co., New York 1929. Price $4.00.

This is a text-book which is intermediate in grade between the elementary and the advanced optics texts. A small amount of differential calculus is used, but otherwise the mathematics required consists of the usual trigonometry, algebra, and geometry. A large number of problems are given, the answers to which are found at the end of the book. Several problems are solved in great detail in the text.

A very commendable feature is the use of photographic illustrations of the various optical phenomena such as interference and diffraction bands, and spectra. These show the various types of band systems obtained with different types of apparatus, giving the student a clear impression of the phenomena under discussion. The photographs are all good except the one of interference rings in polarized light.

In trying to be neither too conservative, nor radical, the author seems to overemphasize the conflict between the corpuscular and wave theories of light. Naturally, most of the phenomena treated require the wave theory. The nature of waves and the composition of vibrations is fully and clearly discussed in an early chapter. The principles thus established are later applied to the treatment of interference, diffraction, and elliptical polarization. The Cornu spiral is explained in a graphical, qualitative manner, and is used to explain some of the Fresnel diffraction phenomena.

The quantum theory and the foundations of Bohr's theory of spectra are briefly reviewed. There are also a few paragraphs on wave mechanics and the diffraction of electron waves, which give a rather belated suggestion of the duality of radiation as well as matter. Optical phenomena due to motion are discussed in the closing chapter.

JOSEPH VALASEK

Elementary Differential Equations. THORNTON C. FRY. Pp. x+255, figs. 42. New York, D. Van Nostrand Co., 1929. Price, $2.50.

This textbook gives a pleasing treatment of its subject of the grade of difficulty that is adapted to junior courses in the better American engineering colleges. It is distinguished by careful presentation of the fundamentals, recognizing that while applications of the subject in physics and engineering are of the highest value, nevertheless, "They are not without their danger, however, if they are used unwisely, for should the student come to rely upon his physical intuition as a substitute for abstract logic, rather than as an aid to it, he would have missed half the benefit of the study." (Preface).

There is a good treatment of operational methods of handling linear equations with constant coefficients, and systems of them, with emphasis on the applications to electrical circuit theory.

E. U. CONDON

Die Grundlage der allgemeinen Relativitätstheorie. A. EINSTEIN. Pp. 64. Fifth unaltered printing. J. A. Barth. Leipzig, 1929.

This is a fifth unaltered printing of Einstein's famous 1916 treatment of the foundations of the general theory of relativity. It was first published, except for the table of contents, as a single article in volume 49 of the Annalen der Physik, and was the first systematic treatment of general relativity, providing the complete mathematical and theoretical foundation leading to the three tests of the theory furnished by the rotation of the perihelion of Mercury, the bending of light in passing through the gravitational field of the sun, and the red shift for light from the surface of the sun. The paper is not only a document of the greatest historical interest, but also still furnishes one of the best introductions to general relativity and contains the three conclusions of the theory for which we have the most direct experimental evidence.

RICHARD C. TOLMAN